

Recent Advances in Green Synthesis of TiO₂ Nanoparticles: Mechanisms, and Applications

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ABSTRACT

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Green synthesis of titanium dioxide (TiO₂) nanoparticles has emerged as a sustainable alternative to conventional chemical methods, offering environmental benefits while maintaining superior performance characteristics. This comprehensive review examines recent advances in plant-mediated synthesis of TiO₂ nanoparticles, focusing on synthesis mechanisms, structural properties, and diverse applications. Various biological extracts including leaf extracts (*Inula viscosa*, *Aloe vera*, *Jatropha curcas*), flower extracts (*Jasminum*, *Magnolia champaca*), fruit peels (*Solanum melongena*, *Citrus sinensis*), and agro-industrial wastes have been successfully employed as bio-reductants and stabilizing agents. The synthesis mechanisms involve complex redox reactions mediated by phytochemicals such as polyphenols, flavonoids, terpenoids, and alkaloids, which serve dual roles as reducing agents and capping ligands. Characterization studies reveal that green synthesis predominantly yields anatase phase TiO₂ with particle sizes ranging from 6-400 nm, depending on the plant source and synthesis conditions. The biogenic nanoparticles demonstrate exceptional photocatalytic performance, achieving complete dye degradation (>99%) within 60 minutes under UV irradiation and enhanced visible light activity compared to conventional TiO₂. Noble metal doping (Au, Ag) further improves performance, with Au/TiO₂ nanocomposites showing 2.5 times higher activity than commercial P25 and remarkable hydrogen evolution rates (468 µmol H₂, 9.3% quantum yield). Applications span environmental remediation, renewable energy production, antimicrobial treatments, and advanced technologies including dye-sensitized solar cells, lithium-ion batteries, and corrosion protection coatings. Despite promising results, challenges remain in batch-to-batch variability and large-scale production standardization. This review consolidates current progress and identifies future research directions toward sustainable, high-performance TiO₂ nanomaterials for environmental and energy applications.

Keywords: green synthesis, titanium dioxide nanoparticles, photocatalysis, plant extracts, environmental remediation

1. INTRODUCTION

Nanotechnology has emerged as a transformative discipline, capitalizing on the unique physicochemical properties of materials at the nanoscale (1–100 nm). At this dimension, materials display enhanced surface-to-volume ratios, quantum confinement effects, and distinctive electronic structures that are absent in their bulk counterparts [1]. Titanium dioxide (TiO₂)

nanoparticles (NPs) have attracted significant research attention due to their superior photocatalytic activity, chemical stability, low toxicity, and cost-effectiveness [2], [3]. Their applications span environmental remediation, self-cleaning surfaces, antimicrobial coatings, hydrogen production, and dye-sensitized solar cells (DSSC) [4], [5]. Among TiO₂ polymorphs—anatase, rutile, and

brookite—the anatase phase demonstrates the highest photocatalytic performance due to its optimal bandgap (~3.2 eV), low recombination rate of photogenerated electron–hole pairs, and high surface energy [1]. However, conventional synthetic techniques, such as sol–gel, hydrothermal, and chemical vapor deposition methods, often involve hazardous solvents, high-energy requirements, and environmentally unfriendly by-products [6]. These limitations underscore the need for sustainable synthetic strategies.

Green synthesis has emerged as a promising alternative to conventional approaches, emphasizing the utilization of renewable biological resources—including plant extracts, microorganisms, and agro-industrial by-products—as reducing and stabilizing agents [2], [7]. This methodology aligns with the principles of green chemistry by minimizing toxic reagent usage, reducing waste generation, and lowering energy input [3]. Plant-based phytochemicals, including flavonoids, phenolics, terpenoids, alkaloids, and polysaccharides, play dual roles during nanoparticle formation: they act as reducing agents to convert titanium precursors into TiO₂ NPs and as capping agents to prevent agglomeration and control morphology [6]. Notably, variations in biomolecular composition significantly influence particle size, crystal phase, surface charge, and optical properties, which ultimately affect photocatalytic efficiency [8]. This biogenic approach offers additional advantages, such as eco-friendliness, cost-effectiveness, and potential scalability, making it suitable for environmental and energy-related applications [4].

Recent advancements in green synthesis have expanded the diversity of biological resources used to produce TiO₂ NPs. Various plant parts—including leaves (*Inula viscosa*), flowers (*Jasminum*), stems (*Tinospora cordifolia*), and fruit peels (*Solanum melongena*)—have been successfully employed as bio-reductants [2], [3], [6]. Moreover, agro-industrial wastes, such as grape pomace rich in anthocyanins and phenolic compounds, have demonstrated excellent potential for nanoparticle synthesis while simultaneously providing a sustainable valorization pathway for agricultural residues [8]. These biomolecules not only facilitate nucleation and crystal growth but also contribute to functional surface modifications that enhance photocatalytic performance, antibacterial activity, and light-harvesting capability [7]. The use of waste-derived biomaterials reflects a paradigm shift towards circular economy practices, integrating

nanotechnology with sustainable resource management. Such advances have laid the groundwork for more sophisticated designs, including doping with noble metals, hybrid composites, and biochar-supported structures to further enhance photocatalytic and optoelectronic properties [4], [5].

The choice of biogenic precursors has a profound influence on nanoparticle morphology, crystallinity, and photocatalytic performance. Each plant extract contains a unique composition of bioactive molecules that dictate nucleation dynamics, particle size distribution, and surface characteristics [6]. For example, *Jasminum* extract has been reported to yield spherical TiO₂ NPs with uniform size, while *Inula viscosa* extract facilitates the formation of highly crystalline anatase particles with excellent optical properties [2], [6]. Likewise, *Solanum melongena* peel extract, rich in flavonoids and anthocyanins, has demonstrated superior capping efficiency, resulting in Au/TiO₂ nanocomposites with narrowed bandgap energy (~2.95 eV) and enhanced hydrogen generation rates [3]. The diversity of phytochemicals allows precise tailoring of electronic structures, making plant-mediated synthesis an adaptable platform for next-generation photocatalysts.

Beyond the choice of biological sources, structural modifications such as metal doping and composite formation have emerged as key strategies to overcome intrinsic limitations of TiO₂, including its wide bandgap and poor absorption in the visible light spectrum [4]. Noble metal doping (e.g., Ag, Au, Pd) induces localized surface plasmon resonance (SPR) effects, which extend the absorption range of TiO₂ into the visible region and facilitate efficient charge separation by creating electron sinks at metal–semiconductor interfaces [3], [7]. For instance, Ag-TiO₂ aerogels synthesized via plant-mediated methods achieved dye degradation efficiencies exceeding 99% within one hour under visible light irradiation [4]. Similarly, Pd/TiO₂ composites prepared using Aloe vera extract demonstrated hydrogen gas release rates (360 mL·min⁻¹·g⁻¹) that significantly surpassed those of chemically synthesized counterparts [9]. These findings highlight the potential of integrating green synthesis with advanced material engineering.

Complementary to metal doping, biochar and silica-supported TiO₂ composites have attracted considerable interest for their enhanced porosity, increased surface area, and improved charge transport properties [6], [8]. Biochar derived from

agricultural residues acts as a conductive network that facilitates electron transfer and mitigates electron–hole recombination, while silica frameworks provide mechanical stability and hierarchical porosity for efficient mass transfer [5]. Moreover, functionalization with organic residues from plant extracts confers additional active sites for pollutant adsorption, thereby synergistically enhancing photocatalytic activity [7]. These hybrid nanostructures demonstrate versatility across diverse applications, including organic dye degradation, photocatalytic hydrogen production, antimicrobial coatings, and energy conversion systems such as DSSCs [4]

When compared to conventional synthesis methods, green routes offer several notable advantages beyond environmental compatibility. TiO₂ NPs produced via sol–gel or hydrothermal methods often require high-temperature calcination and chemical stabilizers, which increase costs and carbon footprints [6]. In contrast, biogenic processes proceed under milder conditions—frequently at ambient temperature and pressure—while generating nanoparticles with smaller sizes (5–50 nm), high crystallinity, and excellent thermal stability [1], [10]. Furthermore, the phytochemical capping agents inherently present on the nanoparticle surface can impart functional properties such as antimicrobial activity and enhanced dye adsorption [7]. These attributes underscore the superiority of green synthesis in meeting the dual demands of high performance and environmental sustainability.

Green-synthesized TiO₂ nanoparticles have been extensively evaluated for applications in environmental remediation, renewable energy production, and antimicrobial technologies. In dye degradation studies, these nanoparticles have shown nearly complete removal of contaminants such as methylene blue, rhodamine B, and crystal violet under visible light irradiation within short reaction times [4], [6]. Their superior photocatalytic efficiency can be attributed to the synergistic effects of nanoscale morphology, high surface area, and bio-derived functional groups that facilitate electron transfer and pollutant adsorption [7]. Additionally, hydrogen production via photocatalytic water splitting has been significantly improved through noble metal doping and plant-mediated surface functionalization [3]. Beyond environmental and energy applications, green-synthesized TiO₂ also exhibits broad-spectrum antibacterial properties, making it suitable for use in medical textiles, coatings, and water disinfection systems [8]

Despite these promising outcomes, several critical challenges remain to be addressed to facilitate the commercial deployment of green-synthesized TiO₂ nanoparticles. One major limitation lies in the batch-to-batch variability of plant extracts, which leads to inconsistencies in nanoparticle morphology, crystallinity, and optical properties [5]. Moreover, large-scale production requires process standardization, reliable quality control measures, and the development of cost-effective downstream purification methods [6]. Advanced characterization techniques, coupled with machine learning algorithms, have been proposed to monitor synthesis parameters in real time and optimize reaction conditions for consistent quality [5]. Addressing these challenges will be critical to transitioning from laboratory-scale demonstrations to industrial applications.

This review aims to provide a comprehensive account of recent advances in green synthesis of TiO₂ nanoparticles, focusing on synthesis strategies, formation mechanisms, and their influence on structural, optical, and photocatalytic properties. Special attention is given to innovations in bio-mediated processes, including metal doping, composite formation, and surface functionalization, that have led to significant performance enhancements in environmental, energy, and antimicrobial applications [2], [3], [4]. Furthermore, the review identifies key challenges and future research directions, highlighting the need for scalable, reproducible, and economically viable synthesis pathways. By consolidating the latest progress, this work seeks to guide future investigations toward the rational design of high-performance TiO₂ nanomaterials produced via environmentally benign methods.

The green synthesis of TiO₂ nanoparticles (NPs) utilizing biological extracts has emerged as a sustainable and efficient alternative to conventional chemical methods. This section provides a comprehensive analysis of the synthesis mechanisms, physicochemical properties, and diverse catalytic and functional applications of these biogenic nanomaterials, drawing from a wide body of recent literature.

2. Mechanistic Pathways and Biomolecular Capping

The formation of TiO₂ NPs via green synthesis is governed by complex redox reactions and stabilization processes mediated by phytochemicals present in plant extracts. Polyphenols, flavonoids,

terpenoids, and alkaloids act as multifunctional agents, serving simultaneously as reducing agents, capping ligands, and structure-directing templates [11], [12]. The reduction mechanism typically involves electron donation from hydroxyl (-OH) and carbonyl (C=O) groups of these biomolecules to Ti⁴⁺ ions, facilitating their nucleation and subsequent growth into TiO₂ NPs. Fourier-transform infrared (FTIR) spectroscopy consistently confirms the involvement of these functional groups, with characteristic signatures observed at 3200–3600

cm⁻¹ (O-H stretching), 1600–1700 cm⁻¹ (C=O stretching), and N-H bending vibrations, which are crucial for nanoparticle stabilization [13], [14]. For instance, the high polyphenolic content in *Citrus sinensis* (orange) peel extract effectively reduced titanium tetrachloride under mild conditions (75°C, pH 6.5), yielding uniform anatase NPs with enhanced photocatalytic activity [15], [16]. The concentration and specific composition of these phytochemicals directly influence the nucleation kinetics and final particle size, as demonstrated by *Inula viscosa* leaf extract, which confined TiO₂ growth to ultra-small particles of 9–18 nm [17].

Table 1: Representative overview of plant-mediated TiO₂ nanoparticle synthesis, characteristics, and applications.

Biological Extract	Precursor of TiO ₂	Particle size (nm)	Application	Phase	Ref
<i>Bixa orellana</i>	Titanium (IV) butoxide	-	DSSC	Anatase	[18]
<i>Jatropha curcas L.</i>	-	25–100	Photocatalysis	-	[19]
<i>Aloe Vera</i>	Titanium (IV) isopropoxide	6–13	Degradasi picric acid	Anatase	[9]
<i>Jasminum, Magnolia champaca</i>	Titanium tetra-isopropoxide	-	Optical (PL), Photocatalysis	Rutile (green), Anatase (chemical)	[1]
<i>Echinophora cinerea</i>	-	244.7	Toxicity assessment	-	[20]
bacterial culture	-	15.23–97.28	Degradation Reactive Red 31	-	[21]
<i>Glycyrrhiza glabra</i>	Titanium oxysulfate	69	Antibactari, anticancer	Anatase	[22]
<i>Cucurbita pepo</i>	Titanium trichloride (TiCl ₃)	-	Photocatalytic	-	[23]
<i>Aloe Vera</i>	-	-	Catalyst Hydrogenation	-	[9]
<i>Trigonella foenum-graecum</i>	-	20–90	Antimicroba	Anatase	[24]
<i>Alhagi maurorum</i>	-	52.24	Degradation Methylene Blue, Antimicroba	Anatase (Ag-doped)	[4]
<i>Solanum melongena L.</i>	-	-	H2 Production	Anatase + Rutile + Au fcc	[3]
<i>Inula viscosa</i>	-	9–18	Degradation MB & Tartrazine)	Anatase	[6]
<i>Cinnamomum tamala</i>	-	-	Degradation methyl orange)	Anatase + Au	[25]
<i>Jatropha curcas L.</i>	-	-	Degradation limbah	Anatase	[26]

<i>Cymbopogon citratus</i>	-	11.96 (TiO ₂), 41.8 (Ag-TiO ₂)	Degradation Mb, Antimicroba	Anatase (TiO ₂), Anatase + Ag	[7].
Pink grape pomace	-	≈13	UV Protection	TiO ₂ nanoparticles	[8]
<i>Citrus sinensis</i>	TiCl ₄	-	Antibacteri	Anatase	[27].
<i>Citrus sinensis</i>	-	31.6–393	Optic Application	Anatase	[28]
<i>Syzygium cumini</i>	-	~10–30	Pb ²⁺ Removal	Anatase	[29]
<i>Acorus calamus</i>	TTIP	15–40	Degradation Rhodamine B, antimicroba	Anatase	[30]
<i>Hibiscus rosa-sinensis</i>	-	-	Degradation Phenol	Anatase	[31]
<i>Aloe vera</i>	-	20–40	Environmental Remediation	Anatase	[32]
<i>Syzygium cumini</i>	Leaf extract	~10-30	Pb ²⁺ & COD removal	Anatase	[29]
<i>Alhagi maurorum</i>	Aerogel preparation	52.24	MB degradation, Antimicrobial	Ag-doped Anatase	[4]
<i>Solanum melongena L.</i>	Hydrothermal	-	H ₂ production	Anatase/Rutile/Au	[33]
<i>Cicer arietinum L.</i>	Biomediated	-	Li-ion battery anode	Anatase/Rutile	[34]
<i>Cinnamomum tamala</i>	Green synthesis	-	Methyl orange degradation	Anatase/Au	[14]
<i>Moringa oleifera</i>	Leaf extract	12.22	DSSC, Photocatalysis, Antibacterial	Anatase	[35]
<i>Plumeria rubra L.</i>	Sol-gel	-	Anticorrosive coating	Anatase	[36]

Beyond conventional photocatalytic and antimicrobial applications, green-synthesized TiO₂ nanoparticles demonstrate remarkable versatility in advanced technological applications. Textile functionalization represents an innovative application where grape pomace extract-derived TiO₂ nanoparticles (≈13 nm) successfully impart multiple functionalities to cotton fabrics, including natural coloration, UV protection, and antibacterial properties [8]. This application exemplifies the circular economy approach by converting winemaking waste into value-added nanomaterials for the textile industry. Corrosion protection applications demonstrate significant industrial potential. *Plumeria rubra* leaf extract-mediated TiO₂ incorporated into epoxy coatings provides exceptional anticorrosive performance on iron substrates [36]. These TiO₂-enhanced coatings demonstrate remarkable resistance to harsh

chemical environments including NaCl, H₂SO₄, and NaOH solutions, highlighting their durability for industrial infrastructure protection. The sol-gel based green synthesis approach ensures uniform distribution of TiO₂ nanoparticles within the coating matrix, optimizing protective performance.

Sensing applications present another frontier for green-synthesized TiO₂. Orange peel extract-derived nanoparticles demonstrate responsive electrical properties as humidity sensors, with the natural surface chemistry imparted by citrus phytochemicals potentially enhancing sensor selectivity and stability [11]. This multifunctional capability, combined with antibacterial and anticancer properties, positions these materials as versatile platforms for smart sensing applications. The bacterial biosynthesis approach using *Bacillus amyloliquefaciens* offers unique advantages for

textile industry applications, particularly in Reactive Red 31 dye degradation [21]. The broad size distribution (15.23-97.28 nm) provides multiple active site configurations, enabling effective degradation of complex textile dyes that may require different particle sizes for optimal interaction# Results and Discussion

3. Synthesis Mechanisms and Biomolecular Interactions

The mechanistic pathways underlying green synthesis of TiO₂ nanoparticles involve complex interactions between phytochemicals and titanium precursors. Our comprehensive analysis reveals that polyphenols, flavonoids, terpenoids, and alkaloids present in plant extracts function as multifunctional agents, simultaneously serving as reducing agents, stabilizers, and morphology-directing templates [15], [37]. The reduction mechanism typically involves electron donation from hydroxyl groups (-OH) and carbonyl groups (C=O) of phytochemicals to Ti⁴⁺ ions, facilitating their conversion to TiO₂. Different titanium precursors show varying reactivity patterns: titanium tetrachloride (TiCl₄) demonstrates rapid reduction kinetics with *Citrus sinensis* peel extract [28], while titanium (IV) butoxide shows more controlled nucleation with *Bixa orellana* seed extract, making it particularly suitable for dye-sensitized solar cell applications [23]. The bacterial biosynthesis using *Bacillus amyloliquefaciens* culture presents an alternative pathway where enzymatic reduction produces TiO₂ nanoparticles ranging from 15.23 to 97.28 nm, demonstrating the versatility of biological reducing agents [21].

Importantly, the concentration and composition of phytochemicals directly influence nucleation kinetics and particle growth. *Inula viscosa* leaf extract, containing high concentrations of phenolic compounds, achieved exceptional size control, producing uniform TiO₂ nanoparticles of 9-18 nm with complete methylene blue and tartrazine degradation within 60 minutes under UV irradiation [6]. Similarly, *Citrus sinensis* extract-mediated synthesis showed remarkable particle size variation from 31.6 to 393 nm depending on calcination temperature, indicating that both biological and

thermal factors govern final particle dimensions [28]. The Aloe vera extract demonstrates particular efficacy in producing ultra-small nanoparticles (6-13 nm) under hydrothermal conditions, achieving enhanced visible light activity for picric acid degradation [22].

4. Phase Composition and Crystallographic Analysis

Phase composition analysis reveals that green synthesis predominantly yields anatase TiO₂, which is highly advantageous for photocatalytic applications due to its superior charge separation properties and higher surface energy compared to rutile phase. XRD characterization across multiple studies consistently shows anatase as the dominant phase, with characteristic peaks at $2\theta = 25.3^\circ, 37.8^\circ, 48.0^\circ$, and 54.6° corresponding to (101), (004), (200), and (105) planes, respectively. Interestingly, the choice of plant extract influences phase formation patterns. Studies comparing *Jasminum* and *Magnolia champaca* flower extracts with chemical synthesis reveal a striking difference: green synthesis preferentially produces rutile phase, while chemical methods favor anatase formation [24]. This phase selectivity demonstrates the unique templating effect of specific phytochemicals present in floral extracts. Conversely, most leaf-based extracts including *Syzygium cumini* (Sethy et al., 2020), *Acorus calamus* [30], *Moringa oleifera* [35], and *Hibiscus rosa-sinensis* [31] consistently produce pure anatase phases.

The crystallite size analysis using the Debye-Scherrer equation reveals significant variations depending on the plant source and synthesis conditions. *Moringa oleifera* leaf extract produced exceptionally small crystallites (12.22 nm) with a band gap of 3.9 eV, making them ideal for dye-sensitized solar cell applications [35]. *Jatropha curcas* L. latex extract yielded larger particles (25-100 nm), providing versatility for various photocatalytic reactions [26]. The bacterial biosynthesis approach using *Bacillus amyloliquefaciens* demonstrated the broadest size range (15.23-97.28 nm), offering tunability for specific applications [21]. Noble metal doping studies reveal enhanced phase stability and modified electronic properties. The Au/TiO₂

nanocomposite synthesized using *Solanum melongena* peel extract exhibited a mixed anatase-rutile structure with incorporated gold nanoparticles, reducing the band gap from 3.06 to 2.95 eV and significantly improving hydrogen evolution activity (468 $\mu\text{mol H}_2$ with 9.3% apparent quantum yield) [3]. Similarly, Ag-TiO₂ aerogels from *Alhagi maurorum* extract maintained anatase structure while incorporating silver nanoparticles (52.24 nm), achieving 99.7% methylene blue degradation within 27 minutes [4].

Morphological analysis reveals that green synthesis produces TiO₂ nanoparticles with diverse structures ranging from spherical to quasi-spherical geometries, with size control being strongly dependent on the plant extract type and synthesis conditions. The most remarkable size control was achieved using *Inula viscosa* leaf extract, producing ultra-small nanoparticles (9-18 nm) with exceptional uniformity, enabling complete dye degradation within 60 minutes. Plant source demonstrates significant influence on particle size distribution. *Aloe vera* extract under hydrothermal conditions consistently yields small nanoparticles (6-13 nm for picric acid degradation studies, 20-40 nm for general photocatalytic applications) [22], [32], attributed to the high concentration of bioactive compounds including vitamins and amino acids that act as natural stabilizing agents. *Acorus calamus* leaf extract produces slightly larger globular particles (15-40 nm) with well-defined crystalline boundaries, achieving 96.59% Rhodamine B degradation efficiency [30].

The synthesis approach significantly affects particle size ranges. Room temperature synthesis using *Jatropha curcas* L. leaf extract produces spherical anatase particles optimized for industrial wastewater treatment, achieving 82.26% COD removal and 76.48% chromium elimination [26]. In contrast, the latex-based synthesis from the same plant species yields larger particles (25-100 nm), demonstrating the importance of plant part selection in size control. Doping with noble metals introduces additional morphological complexity while maintaining size control. Ag-doped TiO₂ synthesized using *Cymbopogon citratus*

(lemongrass) extract shows controlled size variation, with pure TiO₂ particles measuring 11.96 nm and Ag-TiO₂ composite particles reaching 41.8 nm [7]. This size increase correlates with enhanced antimicrobial activity and improved methylene blue degradation (96.96% efficiency). Bacterial-mediated synthesis using *Bacillus amyloliquefaciens* demonstrates the broadest size distribution (15.23-97.28 nm), offering tunability through fermentation conditions [21]. This approach provides unique advantages for textile dye degradation applications, where varied particle sizes can address different pollutant molecules effectively.

The influence of synthesis parameters on TiO₂ nanoparticle properties has been systematically investigated across multiple studies. pH emerges as a critical factor, with basic conditions (pH 9) promoting smaller particle sizes and purer crystalline phases compared to acidic or neutral environments. *Hibiscus rosa-sinensis* extract-mediated synthesis demonstrated that alkaline pH enhances hydroxyl ion availability, accelerating titanium precursor hydrolysis and restricting uncontrolled particle growth [31]. Temperature optimization studies reveal a delicate balance between crystallinity and particle size. Lower temperatures (70-80°C) favor smaller particle formation but may result in reduced crystallinity, while higher temperatures promote crystal growth but risk particle agglomeration. Lemon peel extract-based synthesis achieved optimal photocatalytic activity at 75°C and pH 6.5, demonstrating the importance of parameter synchronization [16]. Precursor concentration also significantly affects nanoparticle characteristics. Studies using varying titanium precursor concentrations show that dilute solutions promote uniform nucleation, while concentrated solutions lead to rapid growth and potential agglomeration. The optimal precursor-to-extract ratio varies depending on the phytochemical content of the plant material, requiring empirical optimization for each system.

5. Photocatalytic Performance and Environmental Applications

Green-synthesized TiO₂ nanoparticles demonstrate exceptional photocatalytic performance across diverse environmental applications, often surpassing conventional materials. The ultra-small nanoparticles synthesized using *Inula viscosa* leaf extract (9-18 nm) achieved complete degradation of both methylene blue and tartrazine dyes within 60 minutes under UV irradiation, representing one of the fastest degradation rates reported for biogenic TiO₂ [6]. Visible light photocatalytic activity represents a significant advancement, particularly demonstrated by *Aloe vera*-mediated TiO₂ nanoparticles (6-13 nm) which effectively degraded picric acid under visible light illumination [22]. This enhanced visible light response is attributed to quantum size effects and the presence of oxygen vacancies created during the bio-reduction process. Similarly, *Acorus calamus* leaf extract-derived TiO₂ (15-40 nm) achieved 96.59% Rhodamine B degradation efficiency, demonstrating superior performance compared to many chemically synthesized counterparts [30].

Industrial wastewater treatment applications showcase the practical viability of green-synthesized TiO₂. *Syzygium cumini* extract-derived nanoparticles demonstrated exceptional heavy metal removal capabilities, achieving 82.53% Pb²⁺ removal from industrial effluents [29]. *Jatropha curcas* leaf extract-mediated TiO₂ showed remarkable performance in tannery wastewater treatment, with 82.26% COD removal and 76.48% chromium elimination, validating the technology's industrial scalability [26]. The influence of pH on photocatalytic performance was systematically investigated using *Hibiscus rosa-sinensis* extract-mediated synthesis. Basic conditions (pH 9) produced smaller, more active nanoparticles with enhanced phenol degradation efficiency, demonstrating the importance of synthesis parameter optimization for specific pollutant targets [31].

Noble metal-enhanced systems show remarkable performance improvements. Au/TiO₂

nanocomposites synthesized using *Solanum melongena* peel extract achieved 2.5 times higher methyl orange degradation activity compared to commercial TiO₂ P25 under solar light irradiation [25]. The plasmonic enhancement from gold nanoparticles extends light absorption into the visible region while reducing the band gap from 3.06 to 2.95 eV [3]. Similarly, Ag-TiO₂ aerogels from *Alhagi maurorum* extract demonstrated nearly complete methylene blue degradation (99.7%) within 27 minutes, significantly outperforming undoped systems [4].

6. Energy Applications and Hydrogen Production

The application of green-synthesized TiO₂ in energy conversion technologies demonstrates significant potential for sustainable energy solutions. *Bixa orellana* seed extract-mediated TiO₂ synthesis produced anatase nanoparticles specifically optimized for dye-sensitized solar cell (DSSC) applications, with the unique phytochemical composition enhancing electron transport properties and dye loading capacity [23]. Hydrogen evolution represents a breakthrough application for green-synthesized TiO₂. Au/TiO₂ nanocomposites prepared using *Solanum melongena* (eggplant) peel extract demonstrated exceptional hydrogen production activity, achieving 468 μmol H₂ generation with an impressive apparent quantum yield of 9.3% under visible light irradiation [3]. The gold nanoparticles create a synergistic effect by reducing the band gap from 3.06 to 2.95 eV while providing active sites for water splitting reactions.

Hydrogen storage applications present another innovative energy application. *Aloe vera* extract-mediated TiO₂ nanoparticles serve as effective catalyst support materials for ethylenediamine bisborane dehydrogenation reactions, demonstrating the versatility of biogenic TiO₂ in hydrogen economy applications [9]. This dual capability for both hydrogen generation and storage positions green-synthesized TiO₂ as a key material for comprehensive hydrogen energy systems. Electrochemical energy storage applications show promising results for sustainable battery technologies. Bengal gram (*Cicer arietinum* L.)

extract-mediated TiO₂ demonstrated exceptional performance as lithium-ion battery anodes, maintaining 98% capacity retention after 60 cycles [34]. The natural stabilizers present in the plant extract prevent particle aggregation during cycling, resulting in superior electrochemical stability compared to conventional TiO₂ anodes. This enhanced cycle life, combined with the higher intercalation potential of TiO₂ compared to graphite, offers improved safety by minimizing lithium dendrite formation risks.

7. Antimicrobial and Biomedical Applications

Green-synthesized TiO₂ nanoparticles exhibit superior antimicrobial properties compared to chemically synthesized counterparts, attributed to both photocatalytic activity and synergistic effects from residual phytochemicals. Comprehensive antimicrobial studies demonstrate broad-spectrum activity with notable selectivity patterns between bacterial strains. *Acorus calamus* leaf extract-derived TiO₂ nanoparticles (15-40 nm) showed preferential activity against Gram-positive bacteria including *Bacillus subtilis* and *Staphylococcus aureus* compared to Gram-negative strains [30]. This selectivity is attributed to differences in cell wall structure and the interaction mechanisms between nanoparticles and bacterial membranes. The dual functionality of these nanoparticles, combining 96.59% Rhodamine B degradation efficiency with strong antimicrobial properties, demonstrates their potential for water purification applications.

Citrus sinensis (orange peel) extract-mediated TiO₂ demonstrated multifunctional biomedical properties, showing significant antibacterial activity against both *E. coli* and *S. aureus* while exhibiting selective cytotoxicity against lung cancer cell lines [11]. This selective toxicity profile, combined with acceptable biocompatibility toward normal cells, positions these nanoparticles as promising candidates for cancer therapy applications. Metal-doped systems show enhanced antimicrobial performance through synergistic mechanisms. Ag-TiO₂ nanoparticles synthesized using *Cymbopogon citratus* (lemongrass) extract exhibited dual-action antimicrobial effects, combining TiO₂ photocatalytic

activity with silver-induced oxidative stress [7]. The silver doping increased particle size from 11.96 nm (pure TiO₂) to 41.8 nm (Ag-TiO₂) while significantly enhancing both photocatalytic (96.96% methylene blue degradation) and antimicrobial activities.

Glycyrrhiza glabra root extract-derived TiO₂ nanoparticles (69 nm) demonstrated both antibacterial and anticancer properties, showcasing the versatility of root-based phytochemicals in imparting biomedical functionality [20]. The larger particle size in this system may contribute to sustained release of bioactive compounds, extending the therapeutic window for biomedical applications. Toxicological assessments using *Echinophora cinerea*-mediated TiO₂ (244.7 nm) provide important safety data for aquatic ecosystems [1]. These studies demonstrate that while green synthesis reduces chemical toxicity compared to conventional methods, particle size and concentration effects on aquatic organisms require careful evaluation for environmental applications.

8. Advanced Applications and Emerging Technologies

Beyond conventional photocatalytic and antimicrobial applications, green-synthesized TiO₂ nanoparticles demonstrate remarkable versatility in advanced technological applications. Textile functionalization represents an innovative application where grape pomace extract-derived TiO₂ nanoparticles (\approx 13 nm) successfully impart multiple functionalities to cotton fabrics, including natural coloration, UV protection, and antibacterial properties. This application exemplifies the circular economy approach by converting winemaking waste into value-added nanomaterials for the textile industry. Corrosion protection applications demonstrate significant industrial potential. *Plumeria rubra* leaf extract-mediated TiO₂ incorporated into epoxy coatings provides exceptional anticorrosive performance on iron substrates. These TiO₂-enhanced coatings demonstrate remarkable resistance to harsh chemical environments including NaCl, H₂SO₄, and NaOH solutions, highlighting their durability for

industrial infrastructure protection. The sol-gel based green synthesis approach ensures uniform distribution of TiO₂ nanoparticles within the coating matrix, optimizing protective performance [36].

Sensing applications present another frontier for green-synthesized TiO₂. Orange peel extract-derived nanoparticles demonstrate responsive electrical properties as humidity sensors, with the natural surface chemistry imparted by citrus phytochemicals potentially enhancing sensor selectivity and stability. This multifunctional capability, combined with antibacterial and anticancer properties, positions these materials as versatile platforms for smart sensing applications. The bacterial biosynthesis approach using *Bacillus amyloliquefaciens* offers unique advantages for textile industry applications, particularly in Reactive Red 31 dye degradation [21]. The broad size distribution (15.23-97.28 nm) provides multiple active site configurations, enabling effective degradation of complex textile dyes that may require different particle sizes for optimal interaction and degradation kinetics.

9. Marine Resource Utilization and Novel Synthesis Routes

The utilization of marine resources for TiO₂ synthesis represents an innovative expansion of green synthesis approaches that remains largely unexplored in the current literature. While terrestrial plant extracts dominate the field, marine organisms such as algae contain unique bioactive compounds including fucoidans, alginates, and specialized polyphenols that could enable TiO₂ nanoparticle formation with distinct properties [12]. The high salt content and unique metabolic pathways in marine organisms may influence nanoparticle surface chemistry and morphology, potentially offering opportunities for developing specialized applications in marine environments such as antifouling coatings and seawater treatment systems.

The current research focus on terrestrial plant materials presents opportunities for expanding the

bioresource diversity. Comparative analysis of the reviewed studies shows predominant use of common agricultural plants (*Citrus sinensis*, *Jatropha curcas*, *Aloe vera*) and medicinal herbs (*Glycyrrhiza glabra*, *Trigonella foenum-graecum*), suggesting that exploration of marine-derived biomolecules could reveal novel synthesis pathways and enhance the range of achievable nanoparticle properties. Future investigations into marine biosynthesis could provide sustainable alternatives to terrestrial resources while accessing unique phytochemical profiles not available in land-based plants.

10. Comparative Analysis with Conventional Methods

Systematic comparison between green synthesis and conventional chemical/physical methods reveals distinct advantages of the biogenic approach, as evidenced by the comparative study of *Jasminum* and *Magnolia champaca* flower extracts versus chemical synthesis [24]. This investigation demonstrated fundamental differences in phase formation, with green synthesis producing rutile phase TiO₂ while chemical methods yielded anatase phase, indicating that phytochemicals can direct specific crystal growth pathways not accessible through conventional routes.

The particle size control achievable through green synthesis often surpasses conventional methods. *Inula viscosa* leaf extract-mediated synthesis produced remarkably uniform nanoparticles (9-18 nm) with complete dye degradation capability [6], demonstrating superior size control compared to typical sol-gel or hydrothermal methods which often yield broader size distributions. Similarly, *Moringa oleifera* extract achieved exceptional crystallite size control (12.22 nm) with optimal band gap properties (3.9 eV) for DSSC applications [35].

Performance comparison reveals significant advantages for green-synthesized materials. Au/TiO₂ nanocomposites from eggplant peel extract demonstrated 2.5 times higher photocatalytic activity than commercial TiO₂ P25 for methyl orange

degradation under solar irradiation [25]. This enhanced performance stems from the unique surface chemistry imparted by phytochemicals and the controlled noble metal decoration achieved through bio-reduction processes. Energy consumption analysis demonstrates substantial advantages for green synthesis. Most biogenic processes operate at moderate temperatures (room temperature to 90°C), as demonstrated by *Jatropha curcas* leaf extract synthesis at ambient conditions [26], significantly lower than conventional sol-gel (400-600°C) or physical vapor deposition methods. The hydrothermal green synthesis using *Aloe vera* extract, while requiring elevated temperatures, still operates more efficiently than conventional hydrothermal methods due to the catalytic effect of phytochemicals on nucleation and growth processes [22].

Cost analysis reveals multiple economic advantages: elimination of expensive reducing agents and surfactants, utilization of readily available plant materials, and reduced energy consumption. The bacterial biosynthesis approach using *Bacillus amyloliquefaciens* offers additional advantages through controlled fermentation conditions and potential for large-scale bioreactor production [21].

11. Challenges and Future Perspectives

Despite significant advances demonstrated across the reviewed studies, several challenges remain in scaling green synthesis for industrial applications. The variation in particle sizes observed across different plant sources (ranging from 6-13 nm for *Aloe vera* [22] to 244.7 nm for *Echinophora cinerea* [1]) highlights the batch-to-batch variability challenge inherent in biological synthesis methods. This variability stems from seasonal and geographical differences in phytochemical content, as evidenced by the dramatic size range achieved with *Citrus sinensis* extract (31.6-393 nm) depending on processing conditions [28]. Standardization represents a critical challenge, as demonstrated by the diverse synthesis approaches employed across studies. Room-temperature synthesis (*Jatropha curcas* leaf extract) [26],

hydrothermal conditions (*Aloe vera*) [22], sol-gel methods (*Plumeria rubra*) [36], and bacterial fermentation (*Bacillus amyloliquefaciens*) [21] all produce functional TiO₂ nanoparticles but with vastly different characteristics. Developing standardized protocols that ensure consistent quality while maintaining the advantages of green synthesis requires systematic optimization of extraction methods, precursor concentrations, and reaction conditions.

Scale-up challenges become apparent when considering the diverse plant materials required. The exceptional performance of *Inula viscosa* extract (9-18 nm particles with complete dye degradation) [6] may face supply limitations for large-scale production. Similarly, the seasonal availability of specific plant parts (flowers for *Jasminum* and *Magnolia champaca* [24], fresh latex for *Jatropha curcas*) could constrain continuous production. The bacterial synthesis approach offers potential solutions to these supply chain issues through controlled fermentation, though it requires different infrastructure investments. Resource sustainability emerges as a key consideration, particularly for high-performing extracts like *Alhagi maurorum* for Ag-TiO₂ aerogel production [4] or *Solanum melongena* peels for Au/TiO₂ hydrogen evolution catalysts [3]. The integration of waste valorization approaches, as demonstrated with grape pomace for textile applications [8], provides a sustainable model that could be expanded to other agricultural and food processing wastes.

Future research directions should prioritize mechanistic understanding to enable predictive synthesis design. The contrasting phase formation patterns observed between green synthesis (rutile from floral extracts, anatase from leaf extracts) and chemical methods suggest that specific phytochemical-precursor interactions could be exploited for targeted crystal engineering. Advanced characterization of extract compositions combined with computational modeling could enable rational design of synthesis protocols. Machine learning approaches show promise for addressing variability challenges by correlating phytochemical profiles with nanoparticle properties [4], [38]. Such

approaches could predict optimal synthesis conditions based on extract composition, potentially enabling consistent quality control across different plant sources and seasons.

The mechanistic insights derived from the diverse synthesis approaches reveal complex relationships between phytochemical composition and nanoparticle properties. The contrasting behavior observed between different plant parts from the same species (*Jatropha curcas* leaf extract producing uniform spherical particles for wastewater treatment [26] versus latex extract yielding 25-100 nm particles for photocatalysis) demonstrates the critical role of specific biomolecules in controlling nucleation and growth processes. Advanced characterization across multiple studies reveals that the reduction mechanism involves sequential steps: phytochemical-titanium complex formation, nucleation, and stabilized growth. The exceptional size control achieved with *Inula viscosa* (9-18 nm) [6] and *Moringa oleifera* (12.22 nm) [35] extracts suggests that specific phenolic compounds and flavonoids create optimal reducing environments that prevent uncontrolled particle growth. FTIR analysis consistently shows the involvement of hydroxyl and carbonyl groups in titanium reduction and nanoparticle stabilization [30].

The influence of synthesis conditions on final properties is exemplified by the pH study using *Hibiscus rosa-sinensis* extract, where basic conditions (pH 9) produced smaller, more active particles compared to neutral or acidic environments [31]. This pH dependency, combined with the temperature effects observed in *Citrus sinensis* synthesis (31.6-393 nm range with calcination temperature variation) [28], indicates that precise parameter control is essential for reproducible synthesis. Noble metal incorporation mechanisms reveal additional complexity levels. The Au/TiO₂ system from eggplant peel extract demonstrates simultaneous reduction of both titanium and gold precursors, creating intimate metal-semiconductor interfaces that enhance both photocatalytic activity (2.5× improvement over P25) and hydrogen evolution performance (9.3%

quantum yield) [3], [25]. The Ag-TiO₂ aerogel system shows controlled silver nanoparticle decoration, maintaining the aerogel structure while achieving plasmonic enhancement [4].

Computational approaches are beginning to provide molecular-level insights into these complex processes. Density functional theory calculations could elucidate the binding energies between specific phytochemicals and titanium species, enabling prediction of optimal extract types for target applications. Molecular dynamics simulations could reveal the role of biomolecular assemblies in directing crystal growth and preventing agglomeration. The future optimization strategy should integrate multi-scale modeling approaches with experimental validation. Machine learning algorithms trained on the diverse dataset presented here (spanning particle sizes from 6-393 nm, various phases, and multiple applications) could identify hidden correlations between synthesis parameters and performance metrics [1], [4]. This data-driven approach, combined with mechanistic understanding, promises to transform green synthesis from an empirical art to a predictive science, enabling rational design of next-generation sustainable nanomaterials for catalytic applications.

12. CONCLUSION

The green synthesis of TiO₂ nanoparticles using biological extracts represents a paradigm shift toward sustainable nanomaterial production, successfully addressing the environmental and energy challenges associated with conventional chemical synthesis methods. This comprehensive investigation demonstrates that diverse biological resources, including plant extracts from leaves, flowers, fruit peels, and agro-industrial wastes, can effectively produce TiO₂ nanoparticles with superior characteristics and performance. The mechanistic pathways involving complex interactions between phytochemicals (polyphenols, flavonoids, terpenoids, alkaloids) and titanium precursors enable precise control over nanoparticle size (6-400 nm) and crystal phase formation. The predominant formation of anatase phase through green synthesis provides exceptional photocatalytic activity, achieving >99% dye degradation efficiency within 60 minutes and enhanced visible light performance compared to conventional TiO₂. The unique surface

chemistry imparted by bio-derived capping agents contributes significantly to these enhanced properties.

Strategic innovations through noble metal doping (Au, Ag) and composite formation have yielded remarkable performance enhancements across multiple applications. Au/TiO₂ nanocomposites demonstrate 2.5-fold higher photocatalytic activity than commercial P25 and exceptional hydrogen evolution capabilities (468 $\mu\text{mol H}_2$, 9.3% quantum efficiency), positioning these materials at the forefront of sustainable energy technologies. The versatility of green-synthesized TiO₂ extends beyond traditional photocatalytic applications to advanced technologies including dye-sensitized solar cells, lithium-ion battery anodes, anticorrosive coatings, and antimicrobial systems. These diverse applications validate the technological readiness and commercial potential of biogenic nanomaterials while supporting circular economy principles through waste valorization approaches. Despite significant progress, challenges in batch-to-batch variability and large-scale production standardization require systematic attention. Future research directions should prioritize mechanistic understanding, process standardization, and integration of machine learning approaches for predictive synthesis control. Addressing these challenges will facilitate the transition from laboratory demonstrations to industrial-scale sustainable nanomaterial production, ultimately contributing to environmentally responsible advanced manufacturing processes.

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CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Devi Lestari: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Project administration, Funding acquisition.

Imas Masriah: Methodology, Validation, Investigation, Resources, Data curation, Writing - review & editing, Supervision.

Detailed Contributions:

Devi Lestari contributed to the conceptual framework and research design of this comprehensive review on green synthesis of TiO₂ nanoparticles. She conducted extensive literature investigation across multiple databases, performed systematic data curation and analysis of synthesis methods, characterization techniques, and performance metrics from diverse plant sources. She prepared the original manuscript draft including all sections from introduction through conclusion, created tables and figures for data visualization, and managed the overall project coordination. She also secured funding support for this research initiative.

Imas Masriah provided critical methodology validation and technical supervision throughout the research process. She contributed to the investigation of mechanistic pathways and biomolecular interactions, provided additional resources and expertise in nanomaterials characterization, and conducted thorough review and editing of the manuscript to ensure technical accuracy and scientific rigor. Her supervision ensured the quality and consistency of the analytical approach across all sections of the review.

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