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GREEN SYNTHESIS OF METAL OXIDE NANOPARTICLES AND THEIR PHOTOCATALYTIC PROPERTIES

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Abstract:
A promising method for producing metal oxide nanoparticles (MONPs) with less reliance on dangerous reagents and maybe less environmental impact than other traditional methods is plant-mediated green synthesis. Polyphenols, flavonoids, sugars, organic acids, and proteins found in aqueous extracts from leaves, flowers, fruits, bark, and agricultural residues can take part in metal-ion complexation, hydrolysis, nucleation, growth regulation, and surface stabilization. The manufacture of representative photocatalytic oxides, specifically zinc oxide (ZnO), titanium dioxide (TiO_2), copper oxide (CuO), and iron oxides, as well as the general concepts of plant-assisted synthesis are covered in this paper. Alongside fundamental characterisation techniques such as UV–visible spectroscopy, Fourier-transform infrared spectroscopy, X-ray diffraction, electron microscopy, and surface-area analysis, the relationship between synthesis variables and material properties is taken into consideration. Light absorption, electron-hole production, charge-carrier recombination, and the creation of reactive oxygen species are used to explain the photocatalytic mechanism. The potential of green-synthesised oxides for dye degradation under UV or solar irradiation is demonstrated by recent literature, but it also highlights limits in mineralization assessment, catalyst recovery, cross-study comparability, and real-wastewater validation. To enhance the caliber and environmental significance of upcoming research, a repeatable assessment system is suggested.

Keywords: *ZnO, TiO_2, photocatalysis, green synthesis, metal oxide nanoparticles, plant extract, wastewater treatment, and reactive oxygen species*

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1. INTRODUCTION:

Because their optical, electrical, catalytic, and surface characteristics can differ significantly from those of their bulk counterparts, nanostructured metal oxides are significant functional materials. Sensors, energy conversion, catalysis, and environmental cleanup are some of their uses. Although they may need high temperatures, organic solvents, potent reducing or precipitating agents, and energy-intensive processing, conventional synthesis methods can offer good control over composition and form. When possible, green synthesis uses milder reaction media and renewable biological resources to lessen these impacts [1-3]. The chemical diversity and accessibility of plant extracts make them appealing. Phytochemicals can alter nucleation and crystal formation, coordinate metal ions, affect hydrolysis and condensation, and stay adsorbed on particle surfaces as capping species. Precursor toxicity, extraction solvent, calcination energy, product yield, washing volume, and nanoparticle fate all need to be assessed, therefore the term "green synthesis" should not be taken as evidence of overall sustainability [1,2].

While more recent research has assessed photocatalytic efficacy against model dyes, recent reviews have examined plant-mediated synthesis of Ag2O, CuO, ZnO, MgO, CaO, and TiO_2 [2–5]. The relationship between synthesis, physicochemical characteristics, and photocatalytic performance is the main topic of this paper, with a focus on reporting quality and experimental design.2. Plant-mediated green synthesis: principles and process

A typical synthesis starts with verified plant material, which is then cleaned to get rid of dirt and debris, dried under controlled conditions, reduced in size, and extracted in water or another appropriate low-toxicity solvent. The extract is filtered and combined with an appropriate metal precursor, such as copper salts for CuO, zinc acetate or zinc nitrate for ZnO, or titanium alkoxide or other precursors for TiO_2. Heating and pH modification may encourage hydrolysis, precipitation, and oxide production. To get the desired crystalline oxide phase, the precipitate is separated, cleaned to get rid of soluble residues, dried, and, if needed, calcined.

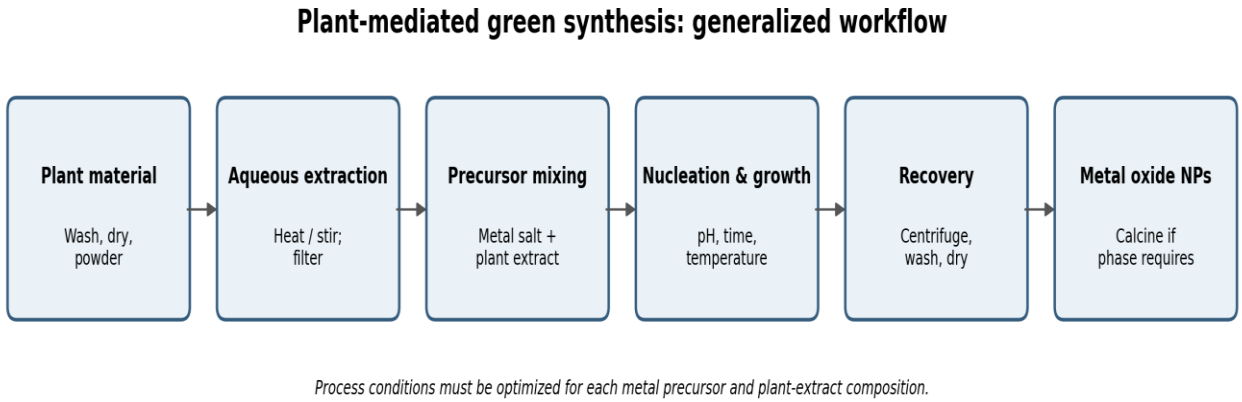

Figure 1. Generalized workflow for plant-mediated synthesis of metal oxide nanoparticles. The exact sequence and calcination requirement depend on the precursor and target oxide.

2.1 Role of phytochemicals

Flavonoids and phenolic substances have carbonyl and hydroxyl groups that can interact with oxide surfaces and metal ions. While organic acids can affect the pH of solutions and the development of metal complexes, proteins and polysaccharides may aid in steric stability. The chemistry of metal oxides frequently involves hydrolysis, complexation, precipitation, and thermal conversion in addition to the straightforward reduction of metal ions to zero-valent metal. Therefore, rather than being deduced from a visual color shift alone, mechanistic claims should be supported by spectroscopy and suitable controls [1,2].2.2 Variables that control product properties

Plant species and plant parts, extraction temperature and duration, extract-to-precursor ratio, precursor concentration, pH, reaction temperature, mixing rate, aging period, and calcination temperature are all significant factors. Nucleation density, crystallite development, aggregation, defect concentration, and surface-bound organic residues can all be affected by changes in any of these variables. One of the biggest obstacles to reproducibility in botanical material is batch-to-batch variability. It is consequently crucial to report plant authentication, the place and season of collection, the extraction yield, and the conditions of extract storage.3. Representative metal oxide photocatalysts

Table no 1 : Representative metal oxide photocatalysts

Material	Useful physicochemical features	Photocatalytic considerations	Common limitations
ZnO	Wurtzite phase, wide-band-gap semiconductor, and reasonably accessible precursors	Beneficial for UV-induced deterioration; flaws and morphology affect activity	Under certain circumstances, photocorrosion or breakdown; restricted absorption of visible light
TiO_2	Chemical stability and a proven rutile/anatase photocatalyst	Strong oxidative chemistry; surface area and phase composition are important	Much of the visible spectrum is limited by a wide band gap, therefore recovery from slurry can be challenging.
CuO	P-type semiconductor with a narrower band gap	can increase absorption to visible wavelengths, which is beneficial for heterojunctions.	Evaluation is necessary for charge recombination, photocorrosion, and copper leaching.
Fe_2O_3 / Fe_3O_4	Iron-based oxides: some phases may be recovered magnetically	Possible solar reaction; magnetic separation could facilitate repurposing	Leaching management and phase purity are crucial; activity is highly dependent on structure.

Among the oxide photocatalysts that are studied the most are ZnO and TiO_2. Iron oxides and CuO are also interesting, especially in heterojunction systems or composites intended to enhance charge separation and visible light sensitivity. The sensitivity of morphology to reaction conditions was noted in a recent analysis that listed plant-extract methods for multiple oxide classes [2].4.

Physicochemical characterization

A UV–visible absorption spectrum alone is insufficient for a compelling photocatalysis investigation. Diffuse reflectance spectroscopy (DRS) is better for predicting optical band gaps of powders, with the selected Tauc exponent and fitting interval supplied; UV–Vis spectroscopy can provide an absorption profile. Functional groups linked to metal-oxygen vibrations and surface residues originating from plants can be found using FTIR. While acknowledging that crystallite size is not equal to particle size, XRD establishes crystalline phase and permits crystallite-size estimation using the Scherrer equation. While EDX offers elemental composition but cannot determine oxidation state on its own, SEM and TEM reveal shape and fundamental particle size. Specific surface area and pore properties can be measured using BET gas adsorption. When accessible, XPS can be used to evaluate surface oxidation states and flaws.

Table no 2 : Physicochemical characterization

Technique	Information obtained	Reporting point
UV–Vis / DRS	Optical response, absorption edge, and estimated band gap	Mode of measurement, baseline, and fitting technique
FTIR	Metal-oxygen vibrations and functional groupings	Report the sample preparation, resolution, and wavenumber range.
XRD	Lattice parameters, crystallinity, and crystal phase	Determine the reference phase and reveal the size and peak-fitting techniques.
SEM / TEM	Particle size, aggregation, and morphology	Give the particle-size distribution and scale bars.
EDX / XPS	Surface chemical states and elemental composition (XPS)	Don't use EDX alone to determine the oxidation state.
BET	Particular porosity and surface area	Describe the adsorption model and degassing conditions.

5. Photocatalytic mechanism

Electrons may be stimulated from the valence band to the conduction band, leaving positively charged holes, when a semiconductor absorbs photons with energy equal to or greater than its effective band gap. These charge carriers have the ability to recombine or move to the surface. Depending on band-edge potentials and solution circumstances, valence-band holes can oxidize water or surface hydroxyl groups to hydroxyl radicals (•OH), while conduction-band electrons can convert dissolved oxygen to superoxide radicals ($\bullet O_2^-$). Under sufficiently oxidative conditions, these reactive species can convert adsorbed organic contaminants into intermediates and eventually mineralize them into carbon dioxide, water, and inorganic ions [3-5].

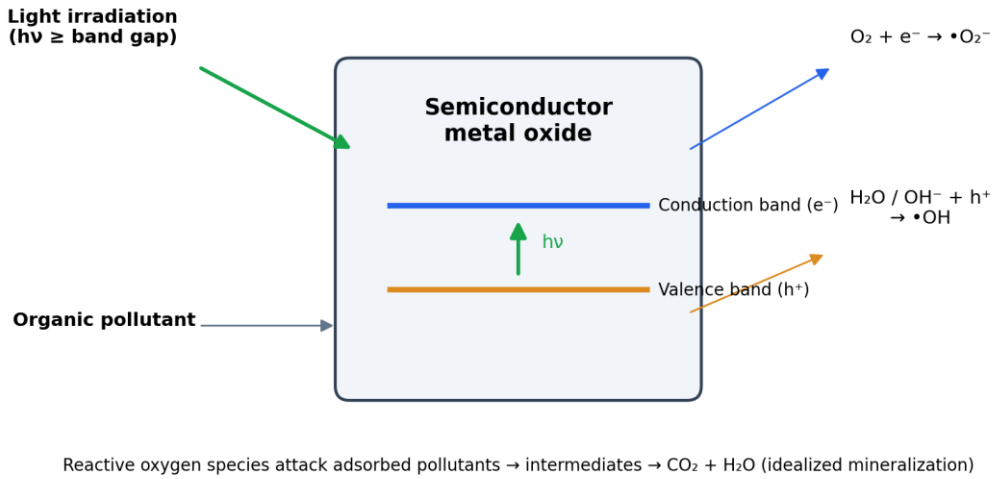

Figure 2. Simplified semiconductor photocatalysis pathway. The specific reactive species and pathway depend on band-edge positions, pH, oxygen availability and pollutant chemistry.

Light spectrum and intensity, catalyst dose, pollutant concentration, pH, dissolved oxygen, temperature, adsorption equilibrium, and reactor design all have an impact on photocatalytic performance. It is best to perform dark adsorption equilibration prior to illumination. To differentiate photocatalysis from direct photolysis and adsorption, a catalyst-free photolysis control and a dark catalyst control are necessary.

6. Research gaps and future perspectives

The application of laboratory photocatalysis in water treatment is limited by a number of problems. First, unlike real industrial effluents, many research use a single synthetic dye at concentrations and water chemistries. Second, differences in illumination intensity, spectral distribution, reactor geometry, catalyst loading, and beginning pollutant concentration make it challenging to compare reported degradation percentages. Third, even though aromatic intermediates might still be present, color loss is frequently utilized as the primary endpoint. Fourth, there is inconsistent evaluation of nanoparticle recovery, metal leaching, ecotoxicity, and performance following multiple cycles. Future research should focus on the following areas: (i) verified, locally accessible plant feedstocks and agricultural residues; (ii) design-of-experiments optimization of synthesis and photocatalysis; (iii) visible-light-active heterostructures with well-characterized band alignment; (iv) immobilized catalysts or magnetic recovery strategies; (v) testing actual wastewater and mixed pollutants; (vi) TOC/COD and intermediate analysis; (vii) leaching and ecotoxicity measurements; and (viii) life-cycle and cost assessment. A direct comparison of the same oxide made from two locally accessible botanical wastes with matched precursor concentrations and regulated calcination, followed by standardized solar-simulator testing, would be a helpful innovation.

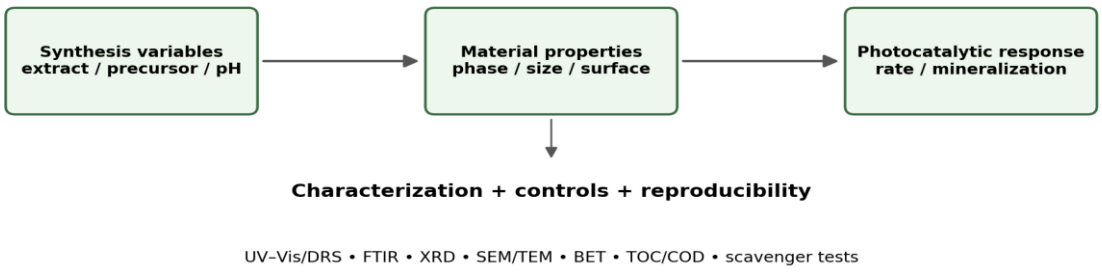

Figure 3. Suggested evidence chain linking synthesis conditions to material properties and photocatalytic response.

7. CONCLUSION:

The quality of the final photocatalyst is dependent on the interaction of extract chemistry, precursor conditions, thermal treatment, and surface structure, whereas plant-mediated green synthesis offers a flexible platform for producing metal oxide nanoparticles. Different optical and chemical properties are offered by ZnO, TiO_2, CuO, and iron oxides; their photocatalytic efficacy must be assessed utilizing controlled illumination, suitable blanks, kinetic analysis, and mineralization proof. Future research that combines reproducible synthesis with thorough material characterisation, real-wastewater testing, catalyst recovery, leaching evaluation, and transparent sustainability analysis will be the strongest.

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