International Journal for Multidisciplinary Research (IJFMR)
E-ISSN: 2582-2160 ● Website: www.ijfmr.com ● Email: editor@ijfmr.com

Reactive Species and Structure Activity Relationships in Green Synthesised Perovskite Oxides for Visible Light Photocatalytic Degradation of Organic Pollutants

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Abstract:
Green-synthesised perovskite oxides offer opportunities to vary composition, morphology and surface chemistry for photocatalytic water treatment. Their performance, however, cannot be explained by pollutant removal alone. This critical review examines how material characterisation, visible-light reaction measurements and reactive-species tests can establish defensible structure–activity relationships, with emphasis on $LaFeO_3$. Selected studies support investigating bio-assisted preparation and interfacial modification, while methodological evidence identifies limitations in dye bleaching, optical-gap estimation and scavenger interpretation. A controlled experimental framework integrates independent synthesis batches, phase and surface measurements, chromatographic pollutant analysis, carbon accounting and complementary species detection. Adsorption, illuminated disappearance and mineralisation are treated as separate endpoints. Scavenger inhibition is interpreted as a conditional system response rather than a numerical contribution from one radical. The synthesis supports a practical measurement strategy but establishes no new catalyst efficiency, rate constant or dominant reactive species. Reliable mechanistic conclusions require agreement between material identity, reaction behaviour and independent pathway evidence.

Keywords: perovskite oxides; green synthesis; visible-light photocatalysis; reactive species; structure–activity relationships; $LaFeO_3$.

1 Introduction:

Photocatalytic water treatment requires evidence of both chemical change and its cause. A declining pollutant concentration may reflect adsorption, transformation or mineralisation. These outcomes have different environmental meanings, and rapid dye decolourisation alone does not demonstrate the destruction of a chemically diverse pollutant mixture.

Oxide perovskites provide a useful platform because related compositions can exhibit different morphologies, substitutions and surface states. The ABO_3 formula describes a compositional family; phase identity and oxidation states must still be established for each preparation. This paper focuses on $LaFeO_3$ to retain a coherent material basis. $LaCoO_3$, $BiFeO_3$ and $SrTiO_3$ remain possible extensions requiring separate validation.

A green synthesis claim should rest on measurable changes in energy, resource use, hazard or waste. Plant extracts may influence precursor mixing and particle development, but washing, drying and calcination also shape the final powder. Botanical origin therefore cannot substitute for a documented synthesis history or environmental comparison.

Mehdizadeh et al. (2020) examined natural additives in $LaFeO_3$ preparation, while Thirumalairajan et al. (2014) investigated floral-like $LaFeO_3$ under visible light. These examples motivate controlled comparisons without establishing a universally superior route or morphology. Reactor conditions and analytical endpoints constrain any comparison between studies.

1.1 Research objectives

The review has four objectives:

1. Identify material measurements needed to interpret activity;
2. Distinguish adsorption, parent-compound conversion and carbon removal;
3. Evaluate evidence for reactive-species assignments;
4. Develop a reproducible design linking synthesis changes to measured properties and reaction behaviour.

2 Review Approach and Evidence Base

Evidence is assessed through material identification, defined irradiation, analytical validity, appropriate controls and consistency between observations and mechanistic claims. Differences in reactors, pollutants and endpoints prevent pooling removal percentages or constructing a reliable cross-study performance ranking.

Table 1 places the principal materials studies beside their relevance. Methodological sources are discussed with the measurements they inform. The supplied manuscript contains no original concentration series, spectra, kinetic estimates or uncertainty data; consequently, no numerical experimental result is reconstructed.

Table 1. Materials evidence retained from the source manuscript

Study	Reported system	Interpretive value
Mehdizadeh et al. (2020)	Bio-assisted $LaFeO_3$ preparation	Preparation can alter morphology, phases and activity; confirm actual phase identity.
Thirumalairajan et al. (2014)	Floral-like $LaFeO_3$ nanosheet assemblies	Architecture can be studied with a defined reaction test; morphology alone does not establish causation.
Al-Nayili and Alhaidry (2024)	$LaFeO_3$ with nitrogen-deficient g-C_3N_4	Adsorption and illuminated removal must be resolved in composite comparisons.

3 Material Design and Green Synthesis

A focused comparison should begin with one parent oxide and change a limited set of variables. The

parent, a compositionally modified sample and a separately defect-adjusted sample address different interventions. A conventional preparation adds a route comparison. Where feasible, a factorial design can distinguish synthesis-route effects from modification effects and their interaction.

Table 2. Proposed comparison groups and their controls

Material group	Comparison	Required qualification
Green parent oxide	Baseline for green-route modifications	Establish actual phase and composition
Green modified oxide	Effect of prespecified substitution	Confirm incorporation and secondary phases
Green defect-adjusted oxide	Effect of a controlled post-treatment	Distinguish defect change from surface or phase change
Matched conventional parent	Route-related comparison	Match precursor ratio and thermal history where feasible
Selected benchmark catalyst	Reactor-level reference	Use identical irradiation and pollutant conditions

For bio-assisted synthesis, document botanical identity, plant part, provenance, extraction conditions and dry-solids concentration. Record precursor purity and hydration, metal ratios, mixing sequence, pH and additive-to-metal ratio. Thermal records must include heating rate, dwell time, atmosphere, sample mass and cooling. These details make batch differences interpretable.

4 Materials and Methods:

4.1 Environmental comparison and replication

Define whether environmental assessment concerns catalyst preparation or the complete treatment process. Preparation-level measures include water and solvent use, isolated yield, energy demand, wash effluent and reagent hazard per unit mass of usable catalyst. Treatment-level assessment also requires catalyst lifetime, recovery and water volume treated to a specified endpoint. Neither is a full life-cycle assessment without the necessary inventory and modelling.

Include extraction, sonication, drying and calcination energy, as applicable, and record failed preparations. A natural additive may reduce one hazard while increasing energy use or organic waste. Comparative evidence should determine how strongly the green designation is supported.

Independent synthesis batches measure preparation reproducibility. Repeated reactors using one batch measure reaction reproducibility, and repeated injections measure analytical precision. These levels must remain separate. Randomise reactor order within practical blocks, repeat a reference material to monitor drift and document exclusions or failed acquisitions. Additional time points do not create independent material replicates.

4.2 Phase composition and morphology

Use powder X-ray diffraction to identify the perovskite and detectable secondary phases. Report acquisition settings, reference patterns and refinement assumptions. A peak shift alone cannot establish uniform dopant incorporation. Peak-broadening estimates describe coherent domains, which should be distinguished from particle dimensions and checked against microscopy.

SEM and TEM should document aggregation and particle distributions through consistently selected fields. Elemental mapping can reveal segregation but cannot independently determine oxidation state or lattice site. Nitrogen sorption provides surface-area and porosity descriptors under stated degassing and analysis conditions; these need not equal the surface available to a hydrated pollutant.

4.3 Optical properties and surface defects

Record diffuse-reflectance spectra under comparable powder packing and reference conditions. Retain the complete spectra and report the transformation, transition assumption, fitting interval and uncertainty used for any optical threshold. Makuła et al. (2018) show why modified photocatalysts require care in band-gap interpretation. An absorption tail is insufficient evidence of a narrowed fundamental gap.

The relationship $E = \frac{hc}{\lambda}$ converts wavelength to photon energy, but an optical onset does not locate both band edges. Electronic-level measurements or justified estimates are required before assigning oxygen-reduction or water-oxidation pathways. Lower steady-state photoluminescence also has several explanations, including absorption changes, trapping and non-radiative relaxation; complementary measurements are needed to connect it with productive chemistry.

For XPS, report calibration, background treatment, fitting constraints and reproducibility. Surface-sensitive information must be distinguished from bulk composition. O 1s components can reflect hydroxyls, adsorbates and carbon-containing species as well as oxygen-related defects. A high-binding-energy component alone cannot quantify oxygen vacancies.

Combine independent defect indicators appropriate to the material, such as EPR, controlled-atmosphere mass changes, oxidation-state analysis or reversible oxygen-treatment comparisons. Claims should follow the combined evidence rather than assign an unsupported absolute vacancy concentration.

4.4 Pollutant analysis

Pair a dye relevant to the application with a suitable non-dye comparator where feasible. Phenol is a candidate supported by the $LaFeO_3$-composite literature discussed here. Characterise substrate absorption over the irradiation range and validate chromatography for parent-compound concentration. Retain UV–visible spectra as supporting evidence. Yan et al. (2006) and Bae et al. (2014) explain why dye sensitisation and decolourisation can complicate activity assessment.

4.5 Reactor conditions and essential controls

Document reactor geometry, working volume, catalyst concentration, suspension, mixing and temperature. Report lamp spectrum, filter transmission, source distance, illuminated area and irradiance at the relevant position. Electrical lamp power does not measure photons reaching the suspension. Check ultraviolet leakage when visible-light filters are used.

Keep gas transfer, headspace and stirring comparable across materials. Catalyst loading influences scattering and penetration as well as surface availability. Where photon flux is quantified, state the method, bandwidth and whether a reported photonic metric uses incident or absorbed photons. Parent disappearance alone does not establish the electron stoichiometry of complete mineralisation.

Follow dark adsorption until a prespecified concentration-stability criterion is met. Keep the prepared concentration separate from the measured concentration at illumination onset. Table 3 identifies controls needed before interpreting illuminated removal.

Table 3. Controls and the competing explanations they address

Condition	Interpretive role
Pollutant in dark without catalyst	Background stability
Pollutant under light without catalyst	Direct photolysis
Pollutant with catalyst in dark	Adsorption and dark reactions
Pollutant with catalyst under light	Combined illuminated response
Catalyst without pollutant	Released species and analytical interference
Additive controls with and without catalyst	Scavenger interference and non-selective effects

If peroxide is added to an Fe-containing system, identify that condition explicitly and include corresponding dark, light and dissolved-metal controls. It must remain distinguishable from oxidant-free photocatalysis.

4.6 Reactive species and transformation products

Scavenger experiments should begin with compatibility checks. Use a concentration series and measure pH, ionic strength, dark adsorption and analytical interference. Include illuminated pollutant–additive tests without catalyst. An alcohol, quinone or electron donor may perturb hydroxyl-associated, oxygen-reduction-related or hole-associated chemistry, respectively, but none should be assumed perfectly selective.

Schneider et al. (2020) demonstrate the interpretive limits of chemical scavenging. Inhibition establishes a system response to an additive, not a direct percentage contribution from one species. Additive effects may overlap and must not be summed into a pathway-contribution pie chart.

Compare air-equilibrated, oxygen-enriched and oxygen-depleted conditions while recording dissolved oxygen. Keep mixing and evaporation comparable. Oxygen dependence can reflect electron acceptance or intermediate chemistry, so it requires interpretation alongside other measurements.

Light-dependent spin-trapping EPR can provide complementary evidence when dark, catalyst-free and reagent blanks are included. Report spin trap, solvent, atmosphere, timing and instrument settings; consider adduct stability and alternative formation routes. A detected species need not control the observed conversion rate.

Ishibashi et al. (2000) provide a TiO_2 precedent for fluorescence-based oxidative-species measurements. Calibration cannot be transferred directly to $LaFeO_3$: probe adsorption, pH, catalyst fluorescence and probe-product degradation require validation in the actual matrix.

Use chromatographic mass spectrometry to investigate transformation products and label uncertain assignments as tentative. Measure total organic carbon separately, allowing for catalyst-derived carbon and adsorption. Carbon loss from filtered water should be described as aqueous TOC removal unless the carbon balance supports a stronger mineralisation claim.

4.7 Kinetics and statistical interpretation

Let C_i denote prepared pollutant concentration, C_0 its measured aqueous concentration after dark equilibration, and C_t its concentration at irradiation time t. Report the two removal stages separately:

$$Dark\ removal\ (\%) = \frac{100(C_i - C^0)}{C_i} \quad (1)$$

$$Illuminated\ removal\ (\%) = \frac{100(C^0 - C_t)}{C^0} \quad (2)$$

Neither quantity independently measures mineralisation. Where an appropriate concentration range supports pseudo-first-order behaviour, fit:

$$C_t = C^0 \exp(-k_{app} t) \quad (3)$$

Here k_{app} has inverse-time units. Inspect residuals, report uncertainty and consider another model when the fit is inadequate. Linearity after transformation does not establish a unique surface mechanism.

An initial mass-normalised disappearance rate can be calculated as:

$$r^0{}_{,m} = k_{app} \frac{C^0 V}{m} \quad (4)$$

V is solution volume and m is catalyst mass. For concentration in mg L^{-1}, volume in L, mass in g and time in min, the rate is mg g^{-1} min^{-1}. Area normalisation uses the measured total catalyst area in place of mass. Both descriptors remain conditional on the reactor and irradiation.

For compatible kinetic fits, the additive-response index is:

$$I_j\,(\%) = 100\left[1 - \frac{k_j}{kref}\right] \quad (5)$$

k_j and kref describe additive and reference conditions. Negative values indicate promotion. Report individual reactor estimates, synthesis-batch means and confidence intervals. A supported mixed-effects model can represent reactors nested within batches. Property–activity associations must use independent batches as the basis of inference.

5 Results and Discussion of Published Evidence

The results of this paper are a critical synthesis, rather than a newly measured catalyst-performance dataset. The literature supports examining preparation, morphology and interfaces while also showing why each apparent improvement needs controls.

Mehdizadeh et al. (2020) link natural-additive preparation to changes in $LaFeO_3$ material properties, including an impurity in one preparation as described in the source manuscript. Phase differences complicate attribution of activity to the intended host oxide. Thirumalairajan et al. (2014) connect a floral-like architecture with a defined visible-light test, but do not establish that this morphology is superior under every spectrum or pollutant condition.

Preparation-related activity should first be examined against phase composition, accessible area and dark uptake. If a difference disappears after appropriate normalisation, increased accessible surface may explain the improvement. That conclusion differs from greater reactivity per comparable surface unit, although both may have practical value.

Al-Nayili and Alhaidry (2024) demonstrate the relevance of $LaFeO_3$–carbon-nitride composites to phenol removal. Because adsorption and photocatalytic behaviour may vary together, component and physical-mixture controls are useful when testing an interface explanation. A composite response cannot automatically be assigned to parent $LaFeO_3$.

Agreement among scavenger response, oxygen manipulation, energetics and independent detection strengthens pathway interpretation. Disagreement may reveal limited sensitivity, short-lived surface chemistry or non-selective additives. Neither inhibition alone nor species detection alone establishes kinetic dominance.

Optical improvement also requires chemical confirmation. Wavelength-dependent reaction measurements and a non-dye comparator can test whether stronger absorption supports productive chemistry. Parent conversion, transformation products and carbon accounting remain separate endpoints. Environmental

interpretation additionally requires catalyst recovery and measurements of relevant released species; one pollutant assay cannot establish complete water safety.

6 Mechanistic Interpretation and Limitations

A conditional mechanism begins with $P + h\nu \rightarrow P(e^-, h^+)$, where P is the photocatalyst. Productive surface reactions compete with recombination and trapping. If energetically supported, $O_2 + e^- \rightarrow O_2^{\bullet -}$ represents an oxygen-reduction step. Holes may oxidise adsorbed pollutants directly; $h^+ + H_2O \rightarrow {}^\bullet OH + H^+$ or $h^+ + OH^- \rightarrow {}^\bullet OH$ are possible hydroxyl-generation steps only where evidence supports them. These expressions are candidate reactions, not confirmed pathways for every $LaFeO_3$ preparation.

Table 4. Evidence required for selected mechanistic claims

Claim	Evidence needed
Useful visible-light response	Reproducible spectra and wavelength-dependent reaction controls
Oxygen-mediated chemistry	Controlled oxygen response and compatible independent detection
Hole or hydroxyl participation	Validated perturbation or detection and plausible energetics
Defect-related improvement	Independent defect indicators and matched batch comparisons
Mineralisation	Carbon accounting with suitable blanks

7 Conclusions:

The review supports matched material comparisons, independent batches, measured illumination, validated chromatography and convergent species tests. It identifies no optimal composition, new rate constant or dominant radical. Its targeted scope and absence of original experiments limit generalisation. Future work should establish reproducibility and separate adsorption from conversion before advancing a fully resolved mechanism.Data availability: No new experimental dataset is reported. Evidence and equations are condensed from the supplied manuscript; literature sources are listed below.

References:

1. Al-Nayili, A., & Alhaidry, W. A. (2024). Novel surface structure of $LaFeO_3$/nitrogen-deficient g-C_3N_4 nanocomposites to improve visible-light photocatalytic performance toward phenol removal. Environmental Science and Pollution Research, 31, 8781–8797. https://doi.org/10.1007/s11356-023-31746-4
2. Bae, S., Kim, S., Lee, S., & Choi, W. (2014). Dye decolorization test for the activity assessment of visible light photocatalysts: Realities and limitations. Catalysis Today, 224, 21–28. https://doi.org/10.1016/j.cattod.2013.12.019
3. Ishibashi, K., Fujishima, A., Watanabe, T., & Hashimoto, K. (2000). Quantum yields of active oxidative species formed on TiO_2 photocatalyst. Journal of Photochemistry and Photobiology A: Chemistry, 134(1–2), 139–142. https://doi.org/10.1016/S1010-6030(00)00264-1

4. Makuła, P., Pacia, M., & Macyk, W. (2018). How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV–Vis spectra. The Journal of Physical Chemistry Letters, 9(23), 6814–6817. https://doi.org/10.1021/acs.jpclett.8b02892
5. Mehdizadeh, P., Amiri, O., Rashki, S., Salavati-Niasari, M., Salimian, M., & Foong, L. K. (2020). Effective removal of organic pollution by using sonochemical prepared $LaFeO_3$ perovskite under visible light. Ultrasonics Sonochemistry, 61, Article 104848. https://doi.org/10.1016/j.ultsonch.2019.104848
6. Schneider, J. T., Firak, D. S., Ribeiro, R. R., & Peralta-Zamora, P. (2020). Use of scavenger agents in heterogeneous photocatalysis: Truths, half-truths, and misinterpretations. Physical Chemistry Chemical Physics, 22(27), 15723–15733. https://doi.org/10.1039/D0CP02411B
7. Yan, X., Ohno, T., Nishijima, K., Abe, R., & Ohtani, B. (2006). Is methylene blue an appropriate substrate for a photocatalytic activity test? A study with visible-light responsive titania. Chemical Physics Letters, 429(4–6), 606–610. https://doi.org/10.1016/j.cplett.2006.08.081