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Review on Green Methods of Photocatalytic Degradation using Nascent Perovskites

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ABSTRACT

In recent times, environmental sustainability has become a global challenge due to the indiscriminate discharge of pollutants into the environment. Environmental pollution, particularly from organic pollutants, poses a significant threat to both ecosystems and human health. The increasing prevalence of these pollutants demands sustainable and efficient solutions. Photocatalytic degradation has emerged as a promising approach for addressing environmental pollution through sustainable and eco-friendly strategies. Among various photocatalytic materials, nascent perovskites have gained significant attention due to their unique structural properties, exceptional optoelectronic characteristics, tunable band gap, and efficient charge transport mechanisms. They have shown considerable potential in catalyzing the degradation of various organic pollutants, including dyes, pharmaceuticals, and other industrial wastes. This review highlights recent advancements in green methods for photocatalytic degradation using nascent perovskites, with an emphasis on their sustainable synthesis, environmental applications, and associated challenges.

Keywords: Synthesis, Perovskite, Photocatalytic, Degradation, Pollutant

INTRODUCTION

Environmental pollution caused by organic contaminants such as dyes, pharmaceuticals, and industrial effluents have become a major global concern. Conventional remediation methods such as chemical oxidation, filtration, and adsorption have limitations in efficiency and sustainability. As a result, they often fail to completely eliminate these pollutants and result in secondary waste. Photocatalysis, an advanced oxidation process driven by light-activated catalysts, has emerged as an efficient and sustainable solution due to its ability to degrade organic pollutants into harmless byproducts (Chen and Zhao, 2021; Joshni and Kalidass, 2011; Chijioke-Okere et al., 2019; Yasmin et al., 2022).

Among the materials explored for photocatalysis, perovskites have attracted significant attention due to their remarkable optical, electronic and catalytic properties. Perovskites are renowned materials of the twenty-first century, which can either be inorganic, organic or organic-inorganic hybrids. The materials are characterized by their distinctive crystal structure, represented by the general formula ABX_3. In this configuration 'A' and 'B' are cations of different sizes, with 'A' being larger than 'B' while 'X' is an anion, typically oxygen or a halide (Xiangshun et al., 2020). While 'A' in the formula is a Group 2 metal ion (Ca, Sr, Ba etc) or f-block metal ion (La, Nd, etc), 'B' is a transition metal ion (Mn, Fe, Cr, Ti, Pb). In an ideal cubic structure, the 'B' cation is octahedrally coordinated by six 'X' anions, forming BX_6 octahedron, while the 'A' cation occupies the interstitial sites, achieving a 12-fold coordination with the 'X' anions (Bhalla et al., 2000). The chemical flexibility of the structure allows possible substitution at either the A or B metal ion sites. Perovskite structure is often predicted by the Goldschmidt tolerance factor (t), calculated as:

$$t = \frac{R_A + R_X}{\sqrt{2(R_B + R_X)}} \quad (1)$$

where R_A, R_B and R_X are the ionic radii of A and B cations, and X anion, respectively.

For a structure to adopt the ideal cubic perovskite form, the tolerance factor typically lies between 0.8 and 1.0. Deviations from this range can lead to cell distortions, resulting in lower symmetries such as tetragonal, orthorhombic, or rhombohedral geometries. Perovskite materials exhibit a rich diversity of structural modifications and variants. These structural variations can significantly influence electronic and magnetic properties, making them a focal point in materials science research (Sicong et al., 2018; Andreja et al., 2022).

In recent years, there has been significant interest in perovskite halides, particularly for their applications in optoelectronic devices like solar cells. The structural properties of these materials, including their dimensionality, and the nature of organic and inorganic components, play a crucial role in determining their stability and performance. For example, the wo-dimensional perovskite halides have been studied for their enhanced stability compared to the three-dimensional counterparts, owing to their unique microstructure characteristics. The materials described by ABX_3 formula, also exhibit other excellent properties such as light absorption, high charge carrier mobility, and tunable band gaps, making them ideal for environmental applications (Zhang et al., 2020).

Furthermore, perovskite oxides with the general ABO_3 formula are well known for their mixed ionic and electron conductivity which makes them suitable for applications such as solid oxide fuel cells and oxygen separation membranes. A critical aspect of their functionality is the transport of oxygen ions (O^{2-}) through the crystal lattice, which plays a key role in maintaining electroneutrality during redox reactions. In perovskite oxide semiconductors, the oxygen ions transport primarily occurs through oxygen vacancy mechanism. The oxygen vacancies help to maintain electroneutrality and to enhance ionic conductivity of oxygen. This means the stability of perovskite structure and its function can be affected by oxygen ion diffusion. Hence, the structure exhibits properties of both ionic and electronic conductivity, with oxygen ions and electrons simultaneously diffusing to neutralize the charges (Dengjie et al., 2015; Möbius et al., 2009). In another scenario, ionic and electronic conductivity properties can be affected by the presence of cations with large ionic radius, consequently, the mobility of oxygen ion is enhanced (Song et al., 2021).

The electronic conduction in perovskite materials is categorized either as an electron conductor (n-type semiconductor) or an electron hole conductor (p-type semiconductor); in which their stabilities vary according to temperature, air, or other oxidizing agents. Perovskite oxides with structural stability are obtained by incorporating oxides of different metals into the crystal lattices to achieve desired ionic transport properties and/or electronic conductivities (Sunarso et al., 2017). The ionic transport properties and/or electronic conductivities of semiconductors is an electron transfer process of nanomaterials that are explored for many important applications in photocatalysis like wastewater degradation, energy production, air cleaning and many others (Hanan and Detlef, 2012). The degradation of a wastewater or dye by photocatalytic process occurs according to the following reaction mechanism:

$$\text{Semiconductor photocatalyst} + h\nu \rightarrow e^-_{cb} + h^+_{vb} \quad (2)$$

Where, e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively.

The equation (2) simply means absorption of UV radiation by photocatalytic semiconductor; induced electron excitation, and promote it from the valence band to conduction band that result to an empty valence band and electron-hole pair. The electron-hole pair then migrates to the catalyst surface, consequently; redox reaction occurs alongside water molecules (Chijioke-Okere et al., 2019; Ajit et al., 2021; Kingsley et al., 2022; Mohamed et al., 2023). Equations 3-7 illustrate the overall reaction mechanism:

$$h^+ + H_2O \rightarrow H^+ + OH^- \quad (3)$$

$h^+ + OH^- \rightarrow OH^\bullet$ 4

$2e^- + O_2 + H_2O \rightarrow H_2O_2$ 5

$e^- + H_2O_2 \rightarrow OH^\bullet + OH^-$ 6

Organic pollutant + $OH^\bullet + O_2 \rightarrow CO_2 + H_2O$ 7

However, concerns regarding the stability of perovskite materials, traditional methods of their synthesis that often involve toxic chemicals and energy-intensive processes, limit their sustainability (Andreja et al., 2022; Liu et al., 2022). To address these issues, researchers are exploring green methods for the synthesis and application of perovskites in photocatalysis. This spurred the narrative review of 102 empirical studies and resulted in a publication focused on recent advancements in green methods of photocatalytic degradation using emerging perovskites, with emphasis on sustainable synthesis, their role in pollutant degradation, and challenges that must be overcome for practical applications.

Green Synthesis of Nascent Perovskites

There are several methods used for the synthesis of perovskite materials. Each method is employed to specific desired outcomes, such as physical, chemical, and optical properties of perovskite materials (Kumar et al., 2020). Aside from the properties mentioned above, these methods also influence key characteristics such as high-purity, ultra-fine, and agglomerate free perovskite nanostructure (Heng and Xinhua, 2016). The methods used to synthesize perovskite materials are described below.

Solvent-Free /Solid-State Syntheses

Conventional methods of synthesizing perovskite often rely on hazardous organic solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Green synthesis methods eliminate or reduce the use of solvents, making perovskite production more sustainable and environmentally friendly techniques (Wang et al., 2023; Gupta et al., 2022). Solvent-free synthesis methods, often referred to as 'solid-state or 'solid-phase' synthesis, involve the direct reaction of solid precursors without the use of solvent medium (Zhao et al., 2022). The technique is subdivided into mechanical ball-milling and high-energy ball-milling methods

Mechanical ball-milling method

In mechanical ball-milling, reactants undergo repeated collisions with milling balls inside a rotating jar; localized heat and pressure are generated to facilitate solid-state reactions (Balaz et al., 2013). The mechanical ball-milling method of synthesis offers advantages such as solvent-free processing, short reaction time, and scalability. The method has been employed to synthesize lead-based and lead-free perovskites such as methylammonium lead tri-iodide ($MAPbI_3$) and cesium tin tri-iodide ($CsSnI_3$) with promising properties for solar cell applications (Zhang et al., 2019). Specifically, Prochowicz et al. (2017) carried out the synthesis of halide perovskite ($MAPbI_3$) from the reaction of methylammonium iodide and lead iodide by milling the precursors to form perovskite ($MAPbI_3$) powder at room temperature. $CsPbBr_3$ nanoparticles can also be synthesized via dry milling precursors CsBr and $PbBr_2$, to produce phase-pure perovskite structure (Kedem et al., 2020).

Perovskite oxides (e.g., $BaTiO_3$ and $SrTiO_3$) were synthesized via the mechanochemical reaction of $BaCO_3$ and TiO_2 by ball milling, followed by calcination at 800 °C to form $BaTiO_3$ (Kumar and Singh, 2019). Similarly, $SrTiO_3$ was synthesized through solid-state milling of $SrCO_3$ and TiO_2; upon subsequent thermal treatment, crystallization was achieved (Chikosha et al., 2015). The mechanical ball-milling technique offers several advantages over conventional methods, including:

- **Solvent-free processing**: Eliminates the need for toxic solvents typically used in wet chemistry, thereby reducing environmental and health risks.
- **Scalability**: Suitable for large-scale production, making it an attractive option for industrial applications.
- **Energy efficiency**: Significantly reduces energy consumption compared to traditional methods, contributing to cost savings and a lower carbon footprint.
- **Rapid synthesis**: Enables short reaction times, accelerating the synthesis process and increasing productivity (Balaz et al., 2013).

However, the method has some limitations, such as agglomeration of nanoparticles and a lack of control over phase purity. As a result, some perovskites require post-milling annealing for complete crystallization. Additionally, halide perovskites are moisture-sensitive and require inert conditions to prevent degradation (Prochowicz et al., 2017; Moreira et al., 2020; Kong et al., 2017).

High energy ball-milling method

This technique involves subjecting the reactants to high-energy impacts from milling balls inside a rotating jar; localized heat and pressure are generated to drive solid-state reactions (Suryanarayana, 2011). High-energy ball milling is widely employed to synthesize perovskite oxides due to its ability to reduce particle size, enhance crystallinity, and improve homogeneity.

$BaTiO_3$ and $SrTiO_3$ perovskites were synthesized by milling $BaCO_3$ (or $SrCO_3$) and TiO_2 at 600 rpm for 2 hours, leading to perovskite phase formation without the need for calcination. This method enhances the dielectric properties of $BaTiO_3$ by reducing grain size between 10–50 nm (Zhang et al., 2019; Ayyappan et al., 2011).

Moreira et al. (2020) reported the synthesis of $LaFeO_3$ and $LaMnO_3$ from La_2O_3 and Fe_2O_3 as starting precursors via the high-energy ball-milling method.

The high-energy ball-milling method has advantages and disadvantages similar to those of mechanochemical ball milling, except that the resulting crystals typically exhibit higher crystallinity.

Aqueous-Based Synthesis Methods

Aqueous synthesis methods utilize water as solvent, which is considered as greener alternative to traditional organic solvents. These methods are simpler and more scalable, offering potential for large-scale production of perovskite nanoparticles (Zhao et al., 2022).

Hydrothermal Synthesis

This method involves the use of water under high pressure and temperature to facilitate the crystallization of perovskite semiconductors. For instance, lead-based halide perovskites like $MAPbX_3$ (X = I, Br, Cl) have been successfully fabricated using the hydrothermal technique (Liu et al., 2021). The fabrication of different perovskite materials has been achieved through this technique. For example, $CsPbBr_3$, a lead halide perovskite, has remarkable optoelectronic applications. Kojima et al. (2009) synthesized $CsPbBr_3$ perovskite by dissolving CsBr and $PbBr_2$ in water and heating in an autoclave at 180 °C for 12 hours. The perovskite crystals formed under these conditions exhibited high luminescence and can be used in light-emitting diodes (LEDs) and solar cells. On the other hand, Rao et al. (2011) fabricated calcium titanate ($CaTiO_3$) by dissolving calcium nitrate ($Ca(NO_3)_2$) and titanium isopropoxide ($Ti(OiPr)_4$) in water, followed by heating at 220 °C for 24 hours in a sealed autoclave. The resulting product showed enhanced dielectric properties. Many other perovskites of similar types have also been successfully produced using the hydrothermal technique.

Hydrothermal techniques have several advantages over other synthetic methods, including high purity, control over particle size and morphology, environmental friendliness, scalability, and cost-effectiveness. These benefits make hydrothermal methods an attractive approach for synthesizing perovskite materials for various applications, particularly in photovoltaics and optoelectronics (Rao et al., 2016; Peng et al., 2017; Xu et al., 2018; Li et al., 2016; Bera et al., 2017).

Despite its merits, the method faces several challenges that hinder its widespread industrial adoption; like difficulties in controlling stoichiometry, achieving reproducibility, managing crystallization kinetics, and scaling the process up to meet industrial demands present a number of challenges. Additionally, issues such as precursor stability and solubility, batch-to-batch variability, long reaction times, and high energy consumption are also drawbacks (Xu et al., 2018; Park et al., 2016; Li et al., 2017; Chen et al., 2019; Zhou et al., 2015; Liu et al., 2017).

Aqueous Sol-Gel Method

Among the synthetic methods for the fabrication of perovskites, the sol-gel method is one of the easiest techniques. It can produce high-quality microstructures and has overcome most of the challenges encountered in other methods, such as texture control, ease of implementation, low cost, low-temperature precursor handling, and the production of high-quality materials with large surface areas (Daniel et al., 2021).

The synthetic route involves the hydrolysis of metal alkoxides in an aqueous solution, followed by gel formation and subsequent heat treatment. The aqueous sol-gel method has been used for the preparation of thin films of Pb-based and other perovskites for optoelectronic devices (Li and Zhang, 2018).

The method includes a subclass known as the sol-gel Pechini method. While the aqueous sol-gel method uses alkoxide salts as reactants, the Pechini method employs metal nitrate salts along with chelating agents (e.g., glycolic acid, citric acid, or EDTA) to ensure the uniform distribution of metals in the final product (Daniel et al., 2021).

Kaewpanha et al. (2019) successfully synthesized Sr-doped $LaFeO_3$ perovskite via the sol-gel Pechini method. The synthesis involved the reaction of lanthanum(III) nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), and strontium(II) nitrate ($Sr(NO_3)_2$) as precursors. Ethylene glycol and citric acid were used as chelating agents to facilitate the formation of the perovskite structure.

Tsaviv et al. (2024) used the sol-gel Pechini technique to fabricate Ni-doped strontium zirconate perovskite nanoparticles. While $Sr(NO_3)_2$, $Zr(OC_3H_7)_4$, and $Ni(NO_3)_2$ were used as precursors, CH_3COOH, EDTA, CH_3CH_2OH, and $C_6H_8O_7$ (citric acid) served as chelating agents. Many other perovskite nanomaterials have also been successfully synthesized using this method.

Auto-combustion

In this technique, a solution of a metal salt—such as oxalates, acetates, or nitrates is prepared by dissolving it in a solvent, typically water or ethanol. Fuels like citric acid and glycine are often used, but urea is the most commonly employed due to its strong exothermic properties and its ability to form a gel-like precursor (Kumar et al., 2020). Kumar and Singh (2019) successfully synthesized $La_{0.7}Sr_{0.3}MnO_3$ perovskite manganite using reactants such as La_2O_3, $SrCO_3$, and $Mn(CH_3COO)_2{\cdot}4H_2O$, with glycine as the organic fuel, through this method.

The auto-combustion method offers several advantages over conventional techniques: (i) No external heat source is required, (ii) High homogeneity and stoichiometric control is achieved, and (iii) Rapid processing enables control over crystalline particle size (Kumar and Singh, 2019).

Despite these advantages, the technique may result in the formation of secondary phases (impurities) due to incomplete combustion or nonstoichiometric reactant ratios. Additionally, agglomeration of particles may occur as a consequence of the rapid combustion process. Furthermore, this method is not environmentally friendly, as the combustion of organic fuels at elevated temperatures can release organic pollutants (Pradhan et al., 2019; Gabal et al., 2019; Shanker et al., 2020).

Co-precipitation method

The co-precipitation method requires soluble metal cations from nitrate salts, ammonium oxalate, urea, ammonium carbonate, hydroxide, acetate, and citrate as raw materials, and cyanides as precipitating agents (Eman, 2019; Helir et al., 2022). The procedure involves dissolving and homogenizing the raw materials in an aqueous medium, followed by the addition of a precipitant (e.g., NH_4OH or NaOH), with the quantity adjusted until precipitation occurs. The resulting precipitate is aged for several hours, then centrifuged, filtered, and washed repeatedly with deionized distilled water and absolute ethanol. The final product can be dried using a thermostatic electric device at a temperature $\leq$ 373 K for approximately 12 hours (Xuehui et al., 2022). The dried product is then calcined at various temperatures to obtain the pure phase of the desired particles (Maulana et al., 2020).

Many perovskite materials, such as $BaZr_{1-x}Y_xO_{3-\delta}$, $LaMn_{1-x}Fe_xO_3$, $LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$, $LaFeO_3$, and $LaGdO_3$, have been successfully prepared using this method (Silvana et al., 2021; Geetha et al., 2018; Wankassama et al., 2018; Chen et al., 2022).

Özkan et al. (2020) synthesized $LaFeO_3$ perovskite powders using the co-precipitation method. They used lanthanum nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$) and iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) as reactants. While citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$) was utilized as a chelating agent, ammonium hydroxide (NH_4OH) served as the precipitation agent. The synthetic procedure of the compound can be visualized from the schematic flow chart shown in Figure 1.

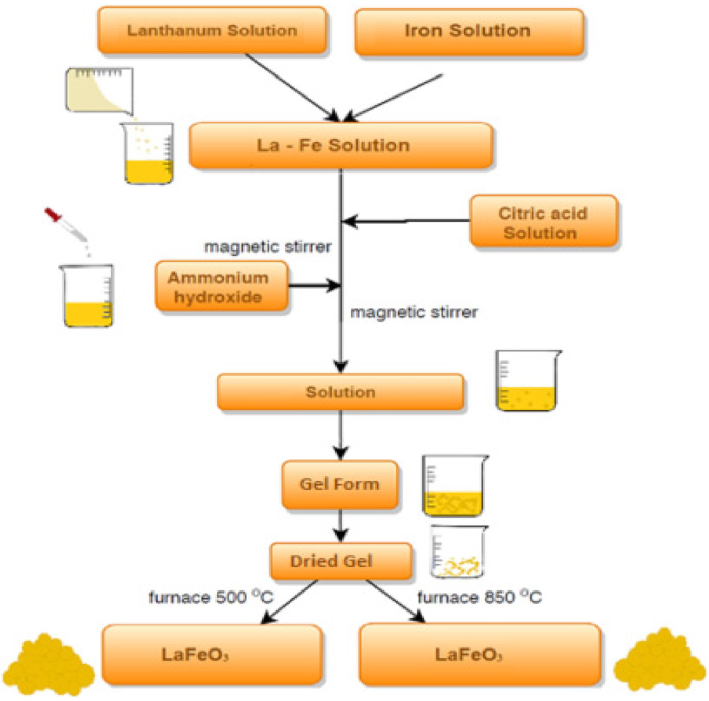

Figure 2: Flow chart for the synthesis of $LaFeO_3$

Co-precipitation method has several advantages over other methods: it reduces reaction energy, is simpler and faster, and avoids the use of hazardous organic solvents, making it more environmentally friendly compared to sol-gel methods (Xin et al., 2019).

However, some limitations may be encountered, including inconsistent phase purity, agglomeration, poor morphology control, lack of stoichiometry and homogeneity control, sensitivity to the precipitant and pH, incomplete precipitation, and low yield (Silvana et al., 2021; Xin et al., 2019; Shilpa, 2024; Amini et al., 2019).

Although green synthesis approaches have succeeded in improving the characteristic parameters of photocatalysts compared to conventional methods (as shown in Table 1).

Table 1: Characteristic parameters of green method and conventional method approach

Parameter	Perovskite	TiO_2	ZnO	Reference
Band gap (eV)	1.5-3.0	3.3	3.4	(a,b,c)
Absorption range	Visible-NIR	UV	UV	(d)
Charge separation	High	Moderate	Moderate	(e,f)
Stability	Moderate	High	Moderate	(g)
Environmental impact	Moderate(except Pb)	Low	Low	(g)

KEY: a = Yaoyao et al., 2021, b = Pasang et al., 2014, c = Jong-Ho et al., 2018, d = Sridevi et al., 2022, e = Chunyi et al., 2024, f = Zafar et al., 2024, g = Wang et al., 2024

Perovskites offer superior light absorption and charge dynamics compared to TiO_2 and ZnO, which may be attributed to their narrow band gap (Wang et al., 2024). However, their environmental impact-particularly due to lead content-remains a challenge. Research into lead-free perovskites, such as $CsSnI_3$ and Bi-based materials, is gaining traction (Das et al., 2023).

Characterization Techniques

X-ray Diffraction (XRD)

XRD is the most common technique used for the structural elucidation of perovskite materials. It allows for the identification of phase purity, crystallinity, and lattice parameters. In the case of nascent perovskites, XRD can detect any residual amorphous phases or impurities that might affect the material's electronic and optical properties (Wang et al., 2018).

The XRD spectra of calcinated perovskite materials are expected to show a single intense peak; however, this is often not the case. Özbay and Yarbay, (2017) reported the XRD patterns of $LaNiO_3$ and $LaMnO_3$, noting a large peak at nearly 32°, which was ascribed to the primary crystalline formation of hexagonal geometry in both compounds, alongside their respective secondary phases. Gabal et al. (2016) reported a similar observation in the XRD pattern of $LaFeO_3$ perovskite. The structural elucidation of $SrPdO_3$ using the XRD technique also confirmed the crystalline formation of a primary orthorhombic perovskite phase, with a secondary phase appearing as a by-product. Lusi et al. (2020) reported the XRD pattern of $CaTiO_3$, indicating an orthorhombic structure and the presence of excess reactants ($CaCO_3$ and TiO_2). The presence of secondary phases in perovskites can often be ascribed to the type of synthetic method employed (Kojima et al., 2009; Peng et al., 2017; Xu et al., 2018; Li et al., 2016; Bera et al., 2017).

FT-IR Spectral Analysis of Perovskite

IR spectra reveal information about the types of functional groups present and the vibrational modes of molecules. They also provide valuable insights into the chemical structure, bonding, and interactions within the material's lattice (Nada et al., 2016). In this review, the spectral analyses of doped $LaNiO_3$ and $LaMnO_3$ perovskites are compared, and the key FT-IR vibrational modes of $LaNiO_3$ and $LaMnO_3$ are summarized in Table 2.

Table 2: FT-IR spectral comparative analysis of $LaNiO_3$ and $LaMnO_3$ [h-p]

Feature	$LaNiO_3$	$LaMnO_3$
Ni-O/Mn-O stretching	550-660 cm^{-1}	500-600 cm^{-1}
Ni-O/Mn-O bending	400-500 cm^{-1}	300-450 cm^{-1}
La-O vibrations	300-400 cm^{-1}	300-350 cm^{-1}
Oxygen vacancy peaks	~600–700 cm^{-1}	~650 cm^{-1}

KEY: h = Liu et al., 2019; i = Joya et al., 2019; j = Kim et al., 2020; k = Zhou et al., 2020; l = Wang et al., 2018; m = Hwang et al., 2018; n = Zhang et al., 2019; o = Zhou et al., 2020; p = Hernandez et al., 2021

The band observed in the $LaNiO_3$ spectrum, in the range of 550–600 cm^{-1}, was assigned to Ni–O stretching, indicating the presence of Ni–O bonds in the perovskite lattice. In the $LaMnO_3$ spectrum, the peak at ~500 cm^{-1} was ascribed to asymmetric stretching of Mn–O, while the frequency at ~600 cm^{-1} was attributed to the symmetric Mn–O stretching mode. The band around 400–500 cm^{-1}, assigned to Ni–O bending modes, is related to the bending motion of the NiO_6 octahedral framework (Joya et al., 2019; Kim et al., 2020; Zhou et al., 2020). Stretching vibrations observed at 300–400 cm^{-1} confirmed La–O bond interactions in the $LaNiO_3$ perovskite structure. The absorption band at ~400–450 cm^{-1}, ascribed to Mn–O bending modes, indicates octahedral deformations in MnO_6. The weak absorption bands in the range of 300–350 cm^{-1} were assigned to La–O stretching modes in the $LaMnO_3$ perovskite nanostructure (Wang et al., 2018; Hwang et al., 2018; Zhang et al., 2019).

New peaks appearing at ~650 cm^{-1} indicate Jahn–Teller distortions in the MnO_6 octahedral geometry after substituting Mn with Fe, Co, or Ni. These substitutions cause shifts in the Mn–O stretching modes, suggesting changes in Mn oxidation states and bond strengths as a consequence of oxygen-deficient structures in $LaMnO_{3-x}$. It was observed that both $LaNiO_3$ and $LaMnO_3$ exhibit metal–oxygen vibrations typical of perovskite structures. However, $LaMnO_3$ is more sensitive to oxygen deficiencies and Jahn–Teller distortions, which strongly influence its FT-IR features (Zhou et al., 2020; Hernandez et al., 2021).

Scanning Electron Microscopy (SEM) Analysis

Scanning Electron Microscopy (SEM) is an analytical technique commonly used to investigate the microstructural properties of perovskite materials such as $LaNiO_3$ and $LaMnO_3$. SEM provides high-resolution images that reveal surface morphology, particle size, porosity, and particle distribution—factors that are critical for understanding a material's properties and potential applications. Bin et al. (2021) reported the surface morphology of $LaNiO_3$ as characterized using SEM. The SEM images revealed crystallites of $LaNiO_3$ perovskite exhibiting a distinctive honeycomb-like nanostructure (Figure 2).

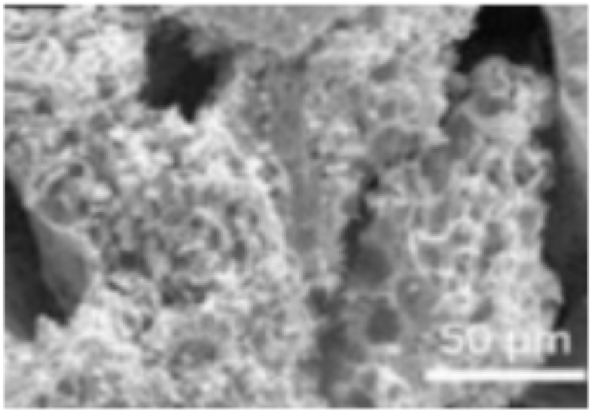

Figure 2: SEM pictorial of $LaNiO_3$

Applications and Photocatalytic Degradation

Nascent perovskites are eco-friendly catalysts that utilize natural, renewable energy sources. They minimize the use of harmful chemicals and, therefore, reduce environmental hazards. These methods have garnered significant interest among researchers due to their ease of use and cost-effectiveness (Abdul et al., 2024).

Owing to their broad light absorption range and efficient charge separation, nascent perovskites have demonstrated remarkable efficiency in breaking down dyes into non-toxic products (Chen et al., 2021). Among these catalysts, nickel-based perovskite ($LaNiO_3$) is a well-known photocatalytic material with excellent performance, attributed to its high conductivity and narrow band gap. $LaNiO_3$ perovskite has been shown to effectively degrade dyes such as methylene blue and rhodamine B under visible light irradiation (Bin et al., 2021). Its honeycomb-like morphology, obtained via a green hydrothermal synthesis, significantly enhances its photocatalytic performance by providing more active sites for dye degradation (Xie et al., 2020). Manganese-based perovskite ($LaMnO_3$) has also demonstrated excellent photocatalytic properties, due to the mixed valence oxidation states of Mn^{3} and Mn^{4} , which generate reactive oxygen species (ROS) essential for degrading dyes such as rhodamine B and methylene blue (Jung et al., 2020).

Sabeeha et al. (2023) conducted photocatalytic degradation of Malachite Green (MG) dye using $LaFeO_3$ nanostructures dispersed in an MG dye solution, which was stirred constantly under sunlight. The adsorption of MG on the surface of the $LaFeO_3$ nanostructure was attributed to reactive oxygen species (ROS) in the photocatalysis process. The degradation percentage of MG was determined using equation 8.

$$\text{Percentage degradation} = \frac{C_0 + C_t}{C_0} \times 100 \qquad 8$$

Where C_0 = absorption at initial time, C_t = absorption time minutes

The photocatalytic degradation of methylene blue (MB) dye suspended in water was also investigated by Tsaiv et al. (2024) under both dark and visible light irradiation in a photoreactor using a $SrZrO_3$ photocatalyst. Photodegradation of MB under UV-visible light was conducted to determine the residual concentration of the MB dye after dark irradiation. The adsorption capacity (Qt) and degradation efficiency (D %) of $SrZrO_3$ were calculated using Equations 9 and 10, respectively.

$$Q_t = \frac{(C_0 - C_t)V}{1000\,m} \qquad 9$$

Where: Q_t (mg/g) = amount adsorbed at time t, V(cm^{-1}) = volume of the solution, m (g) = mass of photocatalyst

$$(D\ \%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad 10$$

Where: D (%) = percentage degradation efficiency, C_0 and C_t = initial and finalconcentrations (mg/L) at respective given time .

In another scenario, the photodegradation of malachite green (MG) in water using $CsSnBr_3$ and $CsPbBr_3$ perovskite halide catalysts was compared by Bohan et al. (2023). The experiments were conducted in a dark reactor box and irradiated with visible light using a 300 W xenon lamp. This was followed by UV-visible spectral analysis using a U-3900 spectrophotometer at fixed time intervals. The efficacy of $CsSnBr_3$ was found to be relatively low compared to the catalytic performance of the $CsPbBr_3$ catalyst, a consequence of band gap differences between Sn and Pb.

The degradation of dyes and antibiotics—amoxicillin (AMX) and tetracycline (TC)—using $ZnTiO_3$ and La_2MnTiO_6 photocatalysts was carried out by Wei-Yu et al. (2021) and Thanh-Nhu-Ngoc et al. (2024). The activities of the catalysts were studied both in the dark and under light irradiation. The concentrations of AMX, TC, MB, and MO were estimated using UV-Vis spectroscopy. Perovskite materials have been explored not only for the mineralization of dyes but also for the degradation of residues from pharmaceutical effluents (such as antibiotics and anti-inflammatory drugs), which pose significant environmental risks. Lead-free perovskites, such as Cs_2SnCl_6 and Bi-based perovskites, have been investigated for the degradation of such pollutants, offering high photocatalytic efficiency and reduced toxicity (Li et al., 2023).

In addition, for pesticides and other hydrocarbons prevalent in industrial wastewater, emerging perovskites have shown effective and promising potential in catalyzing the mineralization of these complex organic compounds into harmless products (Khan et al., 2022).

Challenges and Future Perspectives

Despite the potential and growing adoption of emerging perovskites for photocatalytic degradation, several challenges remain to be addressed. Hybrid perovskites—particularly lead-based variants—are sensitive to moisture and light, leading to their degradation (Liu et al., 2020). These materials also have other drawbacks, such as a limited ability to degrade insecticides and pesticides, which may compromise the effectiveness of semiconductor photocatalysts under sunlight. In addition, the toxicity of lead-based perovskites remains a significant barrier to their practical application (Shoukat and Muhammad, 2024; Tang et al., 2021). Although nascent perovskite materials are promising, their scalability and cost-effectiveness for industrial applications remain challenging and require further optimization (Zhao et al., 2022).

Hence, future research should focus on designing more stable, non-toxic, and cost-effective perovskite materials to ensure commercial viability. Integrating computational methods and artificial intelligence can accelerate the discovery of novel compositions. Furthermore, combining perovskites with other green materials, such as bio-based polymers, could enhance photocatalytic efficiency while ensuring environmental compatibility. In addition, studies should focus on developing perovskite catalysts with multiple recyclable performances.

CONCLUSION

Green methods for photocatalytic degradation using nascent perovskites offer a promising pathway for addressing environmental pollution. Advances in sustainable green synthesis techniques, coupled with the exceptional catalytic properties of perovskites, have demonstrated their potential in degrading a wide range of organic pollutants. However, addressing challenges related to stability, toxicity, and scalability is critical to unlocking their full potential. To tackle these issues, collaborative efforts between materials scientists, environmental engineers, and policymakers will be essential for achieving a cleaner and more sustainable future.

CONFLICT OF INTEREST

The authors declare no conflict of interest concerning the publication of this paper.

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