

Perovskite Oxides: Syntheses and Perspectives on Their Application for Nitrate Reduction

Ajibola A. Bayode,* Odunayo T. Ore, Esther A. Nnamani, Babajide Sotunde, Daniel T. Koko, Emmanuel I. Unuabonah, Brigitte Helmreich, and Martins O. Omorogie*

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ABSTRACT: Over the decades, the rise in nitrate levels in the ecosystem has posed a serious threat to the continuous existence of humans, fauna, and flora. The deleterious effects of increasing levels of nitrates in the ecosystem have led to adverse health and environmental implications in the form of methemoglobinemia and eutrophication, respectively. Different pathways/routes for the syntheses of perovskites and their oxides were presented in this review. In recent times, electrocatalytic reduction has emerged as the most utilized technique for the conversion of nitrates into ammonia, an industrial feedstock. According to published papers, the efficiency of various perovskites and their oxides used for the electrocatalytic reduction of nitrate achieved a high Faradaic efficiency of 98%. Furthermore, studies published have shown that there is a need to improve the chemical stability of perovskites and their oxides during scale-up applications, as well as their scalability for industrial applications.



1. INTRODUCTION

Over the decades, nitrate compounds have been widely deployed to serve domestic, industrial, and agricultural purposes. Nitrate is an inorganic ion formed because of proton loss from nitric acid and is also the conjugate base of this acid. A molecule of nitrate consists of a nitrogen atom covalently bonded to three oxygen atoms and has the empirical formula NO_3^- . However, organic forms of nitrates have the general molecular formula RONO_2 , where R is the molecular formula of any organic compound.¹ They are a class of ester compounds formed by the reaction of nitric acids with alcohols.¹

Nitrates have been found useful in feeding ruminant animals and plants through nitrogen-based fertilizers. They have also served as essential human nutrients when ingested within safe consumption limits. For industrial purposes, nitrate compounds are used as strong oxidizing agents for manufacturing explosives, as fertilizers for enhancing plant growth, and as feedstock for processes where nitrate sources are required.² Animals are fed with nitrate compounds as a major nitrogen source to make ammonia. Intake of human diets with nitrates helps raise nitric oxide levels in the human bloodstream, which helps regulate blood pressure, heart disease management, and regulation of the nervous systems as well as cardiovascular systems.³ Also, adequate nitrate intake has been identified to help improve eye condition and reduce the risk of age-related

sight deficiencies when reduced into nitrite and nitric oxide, which are important nutrients to the eyes.

Their occurrence in human bodies mainly results from the consumption of vegetables and livestock animals. However, the ingestion of nitrates beyond the safe limit would lead to nitrate poisoning. Nitrate poisoning can be evident after plants are fed with nitrogen-based fertilizers.⁴ It is also evident in ruminant animals following how they consume nitrate-poisoned plants. However, nitrate poisoning could become evident in man because of poor air quality, water pollution, and even consumption of nitrate-poisoned plants and animals.

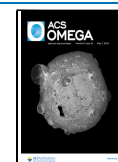
Nitrate deposits are found in both soil and water bodies.⁵ The accumulation of nitrates in soil results majorly from the use of excessive fertilizer, plant decomposition, deposition of animal waste, and runoffs from septic tanks.^{2,6} However, the high solubility of nitrates in water allows them to infiltrate into groundwater or enter surface water through erosion.^{7–9} Hence, wastes from domestic, agricultural, and industrial activities influence the level of nitrates found in ground and surface water.² Effluents from poorly treated sewage plants would also

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be passages for excessive nitrate migration into our water bodies.¹⁰

Plants are the major sources of nitrates and are only found in minute concentrations in animal-based food products. However, nitrate concentration in food sources is generally higher than the observed concentration in water sources.^{5,11} Vegetable plants contain significant concentrations of nitrates, and nearly 80% of human diets are sourced from vegetable consumption.⁵

When nitrates accumulate in water bodies, they become a potential threat to both man and animals who primarily consume water,¹² and health issues such as eutrophication, cancer and methemoglobinemia could result afterward.⁴

The abuse of nitrate intake poses a peril of cancerous diseases to both humans and livestock, as it becomes a cancer vector when ingested excessively. The toxicity of nitrates is measured by the quantity and rate at which it is being ingested. Nitrate ingestion from plant sources (mainly vegetables), animals (meats), and drinking water sources have varying toxic ingestion levels. The accumulation of nitrates in plants has been identified as the root of excessive nitrates ingestion by both man and livestock. This accumulation is a sequel to the effect of low rainfall and unfavorable sunlight conditions that impede the nitrate reductase system from performing significant conversion of nitrates to nitrites.¹³

The accumulation of nitrates in plants harms ruminant animals as it tends to raise the toxicity index of nitrites in their body system. The toxicity index of nitrite will tend to increase when the rate at which nitrates are converted into nitrites becomes much lower than the rate at which nitrites are converted into much-needed ammonia.¹⁴ The absorption of excess concentration of nitrites into the bloodstream of animals impedes the oxygen capacity of their red blood cell, leading to the formation of methemoglobin, a condition that could potentially lead to the termination of their life cycles.

A study reported that there may be a connection between excessive nitrates ingestion from plant vegetables and the development of cancerous growths in the pancreas of humans, but not with ingestion from drinking water sources.¹⁵ On the contrary, the cause of cancer issues related to the bladder was traced to nitrates ingestion from drinking water sources rather than vegetable plant sources.¹⁶ Another study reported that excessive ingestion of nitrates from processed meats may pose the risk of development of cancerous growth in the pancreas, bladders, and breasts of humans who consume them.^{15,17,18}

The ingestion of excessive nitrates from drinking water sources is potentially harmful to both man and livestock. A study reported that women ingesting excessive quantities of nitrates from drinking water sources are prone to suffering cancerous growth in their ovaries.¹⁹ Another study has reported that excessive ingestion of nitrates from drinking water sources raises the tendency of the occurrence of gastric and colon cancers.^{2,7}

Infants (≤ 6 months) are prone to suffer a health condition known as methemoglobinemia, because of ingestion of nitrates from drinking water sources beyond the safe limit.² Pregnant women, as well as women trying to get pregnant, are equally prone to the risk of methemoglobinemia health condition as a result of excessive nitrates ingestion, allowing for malformation of babies in the womb and even undue termination of pregnancies.²⁰

The World Health Organisation (WHO) and the United States Environmental Protection Agency (USEPA) guidelines

have both established $0\text{--}50\text{ mg}\cdot\text{L}^{-1}$ of nitrates concentration as safe limits for both humans and livestock.^{11,20} In contrast, a daily limit of $3.7\text{ mg}\cdot\text{kg}^{-1}$ of nitrates intake has been recommended by the WHO, to avoid excessive nitrates intake.⁵

Nitrates being one of the main essentials of plants, animals, and human diets, cannot be done away with. However, conversion into other innocuous gases such as nitrogen and ammonia can manage their excessiveness. This can be achieved via direct decomposition, selective catalytic reduction, and nitrate storage and reduction methods.²¹

Nitrate reduction processes are essential to environmental sustainability because they reduce nitrate pollution which can have detrimental impacts on ecosystem and human health. One of the main byproducts of nitrate reduction is nitrite (NO_2^-). Sadly, nitrite is poisonous to aquatic life as well as people.²² However, as a fertilizer for plants, ammonium (NH_4^+) has several advantages. However, too much ammonium can cause eutrophication in water bodies, which can upset aquatic ecosystems and result in algal blooms.^{23,24} Nitrate reduction may also result in the release of nitrous oxide (N_2O), a potent greenhouse gas that contributes significantly more to global warming than carbon dioxide.²⁵ Emissions of nitrogen oxide contribute to both climate change and the depletion of the ozone layer. Nitrogen gas (N_2), a harmless and inert gas, is produced when nitrate reduction is completed.^{26,27} Alternatively, an incomplete or inefficient reduction process may cause intermediary nitrogen species, such as nitrite, nitrous oxide (N_2O), and nitric oxide (NO), to accumulate.²⁸ These intermediaries may have detrimental effects on the ecosystem. Improving management strategies via the optimization of process parameters and reducing emissions can mitigate adverse environmental effects and promote the long-term adoption of nitrate reduction technology.²⁹

Since nitrates are very soluble in water, the $\text{N}=\text{O}$ covalent bond thus requires a considerably low energy to break.¹² Some of the technologies that have been deployed to achieve nitrate reduction include photocatalytic, biological, and physical methods.³⁰ Other treatment methods include electrodialysis, ion exchange, and biochemical treatment.⁴ However, the drawbacks associated with some of these techniques have resulted in researchers embracing electrochemical reduction as a more viable alternative for nitrate reduction.⁴ These drawbacks include the cost of pretreatment for electrodialysis, accumulation of brine wastes after ion exchange, and inconvenient operating conditions for biochemical processes.⁴

Electrochemical reduction has been reportedly appraised to be highly efficient and easy to deploy, with lesser demand for adding other chemicals when compared to the techniques mentioned above.⁴ It has also been reported that electrochemical reduction is a more viable green route for achieving biological denitrification and industrial production of ammonia.^{10,12} Also, the electrochemical reduction technique allows for selectivity in either producing nitrogen gas or ammonium, thus providing room for control and flexibility over the desired outcome.³¹ However, the technique is combated with the limitation of poor adsorption of nitrates and the capacity for activating adsorbed nitrates.¹² The efficiency of the electrocatalytic process has been reported to be largely influenced by the rational design of electrocatalysts.^{32,33} Some electrocatalysts reportedly used for the electrochemical reduction of nitrates include noble metal electrodes, non-noble metal

catalysts, bimetallic electrodes, metal compound electrodes, nonmetallic electrodes, and metal-molecular solid catalysts.¹⁰

However, compared to all of the stated electrocatalysts, perovskite oxides, with general molecular formula ABO_3 , have been reportedly identified and appraised for their capacities for achieving significant nitrate reduction, owing to their abilities to facilitate much adsorption of nitrates and significant reduction of the nitrates, which they do by providing more oxygen vacancy sites and allowing partial substitution of their B-site transition metals.^{4,10} It has been stated that perovskite oxides can be generally prepared by microemulsion, spray-drying, freeze-drying, citrate complexation, coprecipitation and sol-gel process.³⁴ While many researchers have appraised perovskites for their capacity to achieve significant nitrates reduction in both lean and rich phase processes, some blocks have been identified as plagues that limit the efficacy of perovskites for electrochemical reduction of nitrates.

Thus, this review reports a comprehensive investigation of the facile syntheses and application of perovskite oxides for nitrates reduction and highlights a research focus geared toward improving the catalytic activity of perovskites for the reduction of nitrates.

2. PEROVSKITES AND PEROVSKITE OXIDES

The development of photocatalyst materials is one of the most promising and thriving answers for a clean and sustainable future, considering its cleanliness, inexhaustibility, efficiency, and affordability. Significant attempts have been made to create enormously operative photocatalyst materials for various applications, including removing carbon dioxide and nitrogen from the air and oxidizing organic water pollutants. In light of this, perovskite photocatalyst materials have gained special attention due to their exceptional properties because of their flexibility and adaptability in chemical composition, structure, bandgap, oxidation, and valence states.³⁵

Perovskites are binary metal oxides with a general formula ABO_3 , where A cation can be a lanthanide, alkaline, or alkaline earth cation, and B cation is a metallic element with 3-, 4-, or 5-day configuration.³⁶ There are several perovskite-related structures on the earth.^{37,38} This is due to their special structural physicochemical characteristics, such as hydrothermal stability, electron mobility, and REDOX behavior. As a result of these distinct features, perovskite and perovskite-related materials have emerged as an important new class of materials, making them very resourceful materials in catalysis, water splitting, solar cells, optical devices, and superconductors.³⁹ Additionally, perovskite oxides can be used in various processes, including those that are liquid at ambient temperature, gas or solid at high temperatures, or under irradiation conditions.⁴⁰

Perovskite oxides are compounds consisting of two or more simple oxides having high melting points.⁴¹ In their ideal form, perovskite oxides are cubic or nearly cubic, like other transition metal oxides containing the same formula (ABO_3).⁴² Phase transitions may happen in some materials at low temperatures. Perovskite oxides have vast potential for many applications due to their structures and crystals, which are simple and exceptional in their ferroelectric and dielectric properties.^{42,43}

A 3-dimensional framework of BO_6 octahedral that share their corners makes up the cubic cell (Figure 1). According to Kubacka et al.,⁴⁴ Peña and Fierro,⁴⁵ and Huang et al.,⁴⁶ the B-site cation is a transition metal component. A group 2 or a rare earth element frequently makes up the A-site cation, which

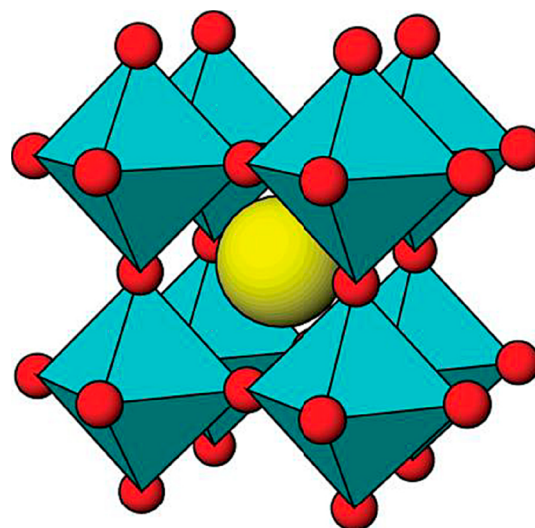


Figure 1. A diagrammatic representation showing the ideal cubic perovskite ABO_3 structure (cyan, BO_6 units; yellow, A atom; red, O atoms).⁴⁴ Reprinted with permission from ref 44. Copyright 2012 American Chemical Society.

resides in the 12-coordinate location created by the BO_6 network. As opposed to the model 3-dimensional perovskite ABO_3 , perovskite-related structures show lattice distortion to varying degrees and result in nonideal structures of the crystal phases like orthogonal, rhombohedral, tetragonal, monoclinic, and triclinic phases. These structures are caused by losing one or more proportional operators in the three-dimensional structure. Although the idealized structure is primitive cubic, the structure can be altered because of the radii of the two cations, which usually involves tilting of the BO_6 units, also known as octahedral tilting.^{44,47–49}

There are three forms of perovskite materials: the first has localized electrons, the second has delocalized energy-band states, and the third can switch between the first two. Perovskite structures come in a variety of forms, including A_2BO_4 layered Perovskite, ABO_3 Perovskite, $A_2A_0B_2B_0'O_9$, Perovskite three and $A_2BB_0'O_6$ Perovskite two.⁵⁰ However, the most abundant ones are $MgSiO_3$ and $FeSiO_3$.⁴³ Oxides and oxides-like types of perovskite have different properties, such as insulator-metal transition, ionic conduction characteristics, dielectric, variation of solid-state phenomena, and metallic and superconducting characteristics.⁴⁵

The structure could have various charge distributions depending on the cations' potential valence and the material's electroneutrality. Therefore, more than 90% of the metallic elements in the periodic table can be used to form perovskite structures.⁵¹ One of the advantages of perovskite structures is the possibility to adopt a wide range of different compositions, changing either the A or the B cation or being partially substituted by other cation(s) of the same or different valence, resulting in a general formula of $A_{1-x}A'_xB_{1-y}B'_yO_{3\pm\delta}$ that can adjust the REDOX, surface, and bulk properties.^{52,53} The stability of the structure depends directly on the geometrical constraints of octahedral or dodecahedral cavities.⁵⁴ Also, the compounds with a formula of AB_2O_4 (A_3O_4 when $A = B$), which is recognized as a spinel structure, possess relatively similar physicochemical properties and are widely used together with ABO_3 for catalysis applications due to their high activity and stability.⁵⁵

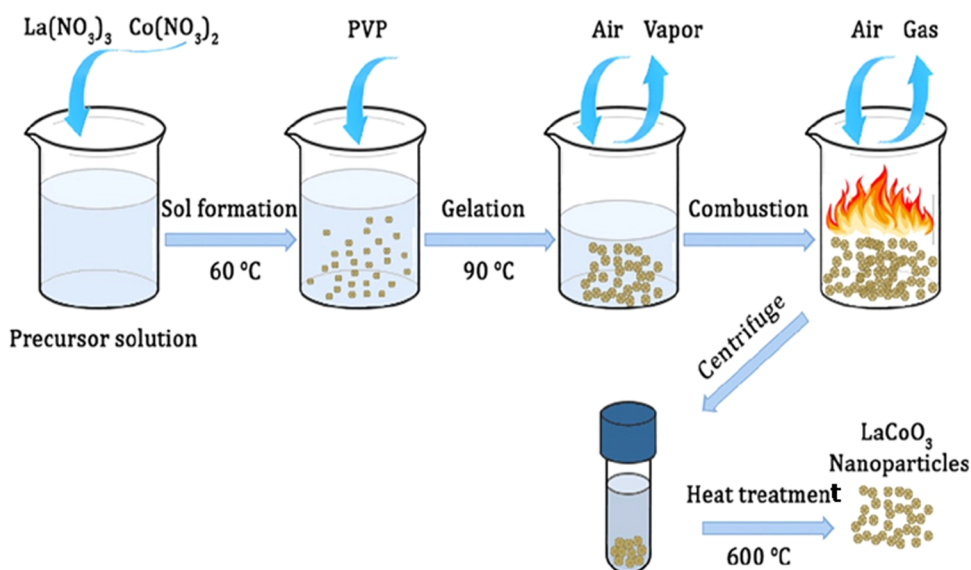


Figure 2. Schematic diagram of the synthesis of LaCoO_3 perovskite oxide using the Autocombustion method.⁷⁰ Reprinted with permission from ref 70. Copyright 2021 John Wiley & Sons Ltd.

The applications of perovskite oxides in heterogeneous catalysis can be dated back to the 1950s by Parravano, who reported the catalytic performance of NaNbO_3 , KNbO_3 , and LaFeO_3 for CO oxidation.^{39,56} The first publications on perovskites, dated the 1970s, reported the exceptional catalytic properties in oxidation reactions and nitric oxide (NO) reduction, suggesting the possibility of replacing platinum-group metals with perovskite in automotive exhaust catalytic converters.⁵⁴

2.1. Classification of Perovskites and Perovskites Oxides. Perovskites and perovskites oxides classification using anion X as the baseline. They include inorganic oxide perovskites, halide perovskites, hydride perovskites, and perovskites hydroxide.^{42,43}

Another important classification is made based on the radii of their metallic ions.⁴³ There are multiple perovskite-based combinations with different physical properties due to the ABO_3 perovskite's malleable crystal structure, capacity to accept a wide variety of cations in various oxidation states, and ability to accept cation or anion vacancies. These features lead to the formation of two key types of oxide phases, namely the ternary ABO_3 type and their solid solutions and the complex modern type compounds $(\text{AB}'_x\text{B}'')_3\text{O}_3$, where B' and B'' are two separate elements in numerous oxidation states and $x + y = 1$. Subsequently, according to their oxidation states, ternary oxides can be further categorized into oxygen and cation-deficient species and $\text{A}^{1+}\text{B}^{5+}\text{O}_3$, $\text{A}^{2+}\text{B}^{4+}\text{O}_3$, $\text{A}^{3+}\text{B}^{3+}\text{O}_3$.⁵⁷

3. SYNTHESIS OF PEROVSKITES AND PEROVSKITES OXIDE MATERIALS

Perovskites are usually formed at increased temperatures because, from their composition, perovskite oxides are compounds consisting of two or more simple oxides having high melting points.^{58,59} The technique used to synthesize perovskite oxide must be selected according to the specific application, specific demands of activity, and selectivity since these depend on how the atoms are arranged on its surface.⁶⁰ It is worth stating that the synthesis techniques also affect the crystal structure and morphology of the synthesized samples.⁶¹ Consequently, the synthesis pathways can be categorized into

three primary divisions: solid-state, liquid-state, and gas-state synthesis. Each method has a distinctive approach. Solid-state methods are used to synthesize bulk materials, liquid-state techniques are used to produce nanomaterials, and gas-state methods are mostly used to fabricate thin films.⁶²

3.1. Solid-State Synthesis Technique. The solid-state synthesis method is commonly used to prepare perovskite in pure form due to the availability of impurity-free precursors, and they find key applications in electronic industries. Researchers most frequently employ this method.⁵⁸ Also, most ceramics are evenly synthesized in this way and are utilized to create polycrystalline materials. This method requires raw carbonate and/or oxide form materials.⁶³ The raw components do not interact chemically in this process at room temperature. However, the chemical reaction occurs quickly when the raw material mixture is heated to very high temperatures (about 700–1500 °C). The downside of the solid-state synthesis approach is that it requires annealing at high temperatures for a long time and frequent intermediary grindings which results in poor homogeneity and difficulty controlling the particle size.^{58,62} Therefore, the problem arises when perovskites from solid-state methods are subjected to surface-related studies.⁶⁴ The different synthesis routes using the solid-state technique are highlighted below.

3.1.1. Mechanical Ball-Milling Method. The mechanical ball-milling method produces solid-state perovskite compounds in bulk. The raw materials are oxides and/or carbonates, which are hand-mixed, ball-milled, and calcined at a high temperature to form perovskite.^{59,62}

3.1.2. High-Speed Ball-Milling Method. The high-speed ball-milling and the mechanical ball-milling methods are very similar. However, the striking distinction between the two techniques is that high-speed ball milling uses a very high rotation per min (rpm). The technique also uses low temperatures to create nanoparticles.⁶⁵ Due to the high likelihood of chemical reactions occurring during high-energy ball-milling, which could produce a variety of harmful gases, this approach only uses metal oxides.^{62,66}

3.2. Liquid-State Synthesis Technique. The liquid-state synthesis is designed to make nanomaterials. Researchers and

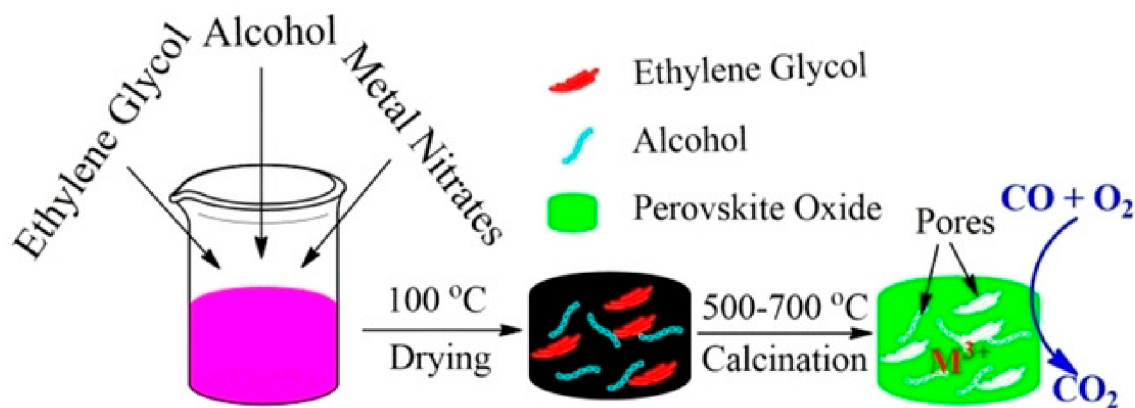


Figure 3. Schematic representation of sol–gel synthesis method for LaCoO_3 perovskite oxide.⁷⁵ Reprinted with permission from ref 75. Copyright 2018 John Wiley & Sons Ltd.

scientists most frequently employ it to create nanoparticles of oxide materials.⁶⁷ Typically, this method utilizes raw materials in nitrates, acetates, or oxalates form. They are combined and expected to react with one another at room temperature. Autocombustion, sol–gel, and coprecipitation are some of the different liquid-state synthesis techniques used to prepare perovskite nanomaterials, which are to be described in more detail.⁴³

3.2.1. Autocombustion Method. The autocombustion method is an easy, low-cost approach for producing perovskite nanomaterials. The starting materials for this method are oxalates, acetates, or nitrates, which are readily soluble in deionized water.⁶² It uses some organic fuel to aid in combustion, such as urea, citric acid, and glycine. In a work by Kumar et al.,⁶⁸ the starting materials La_2O_3 , SrCO_3 , and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were utilized to create $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ perovskite Manganite, with glycine serving as the fuel. La_2O_3 and SrCO_3 were first prepared as nitrates by dissolving them in dilute nitric acid, followed by the dissolution of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and glycine in distilled water to start the reaction. Each of the materials' precursor solutions was independently dissolved and synthesized. At the end, they were mixed while continuously stirred in a big beaker, that was heated on a magnetic stirrer at $175\text{--}200\text{ }^\circ\text{C}$.⁶⁸ After 6–7 h of continuous spinning, the mixed solution thickened and changed into a gel-like structure as seen in Figure 2. As the stirring time increased, an autocombustion occurred, resulting in a flame that emitted a vast array of distinct gases. The temperature of the entire combination increased to $800\text{--}1000\text{ }^\circ\text{C}$ within a short period during the igniting process. The produced blackish-brown powder was removed from the beaker and separated into several portions for calcination at varied temperatures.⁶⁹

3.2.2. Sol–Gel Method. Most chemists produce nanomaterials using the sol–gel technique. This method includes both physical and chemical processes related to the following: hydrolysis, condensation, polymerization, gelation, drying, and densification.⁷¹ This technique uses metal alkoxides as starting materials.⁷² Metal alkoxides typically have a chemical formula of $\text{M}(\text{OR})_x$. They are assumed to be either a derivative of alcohol ROH , where R is an alkyl group or a derivative of metal hydroxide $\text{M}(\text{OH})_x$.^{62,73} A mole ration of metal alkoxides is measured and melted in alcohol or deionized water at $60\text{--}80\text{ }^\circ\text{C}$ under continuous swirling. It is crucial to regulate the pH value of metal alkoxide solutions to prevent precipitation and

to create a homogeneous gel produced by basic or acidic solutions.⁷² Hydrolysis and condensation are two terms used to describe the entire process, which results in the production of polymeric chains. A gel eventually forms because of the development of the polymeric chains, which also causes a noticeable increase in the reaction mixture's thickness as shown in Figure 3. To avoid undesired substances, the gel must be dried between 150 and $200\text{ }^\circ\text{C}$. The resultant gel was annealed at various temperatures between 400 and $800\text{ }^\circ\text{C}$ after removing the contents to produce the pure phased materials.^{64,72} For instance, Andrade et al.⁷⁴ synthesized nanotubes and nanoparticles of $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ perovskite Manganite using the sol–gel method following calcination at different temperatures.⁷⁴ The mole ratio of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, CaCO_3 , and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were utilized for the production of $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ perovskite. To initiate the process, CaCO_3 was dissolved in nitric acid and converted into CaNO_3 , while $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in distilled water. The combinations of all precursors were done using a beaker. As a polymerizing agent polyethylene glycol (PEG) was added in the proper quantity to the precursor solutions. The solution was heated at $70\text{ }^\circ\text{C}$ for 6 h to complete the polymeric development. The solution eventually changed into a thick, yellow gel that could be calcined from 700 to $1000\text{ }^\circ\text{C}$.

3.2.3. Coprecipitation Method. The coprecipitation method requires metal cations from a general medium and precipitates as oxalates, carbonates, citrates, or hydroxides as raw materials.^{62,64} To get the unadulterated phase in the polycrystalline form, the resulting precipitates will have to be calcined at various temperatures after being washed many times with distilled water. With this technique, nearly homogeneous polycrystalline powders can be obtained. For proper precipitation, the solubility of the compounds utilized should be relatively close to one another.⁷⁶ It is essential to remember that the precursor solutions should be mixed at the atomic level to create smaller particles and be calcined at low temperatures to produce a pure material.⁷⁷ Also, the controlling pH of the precursor solution, stirring speed, concentration, and mixture temperature are vital parameters for the coprecipitation method.⁷⁸

The $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0, 0.1, 0.2$) perovskite synthesized by Geetha et al.⁷⁹ is an example of the coprecipitation method.⁷⁹ Mole ratio of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in distilled water. These

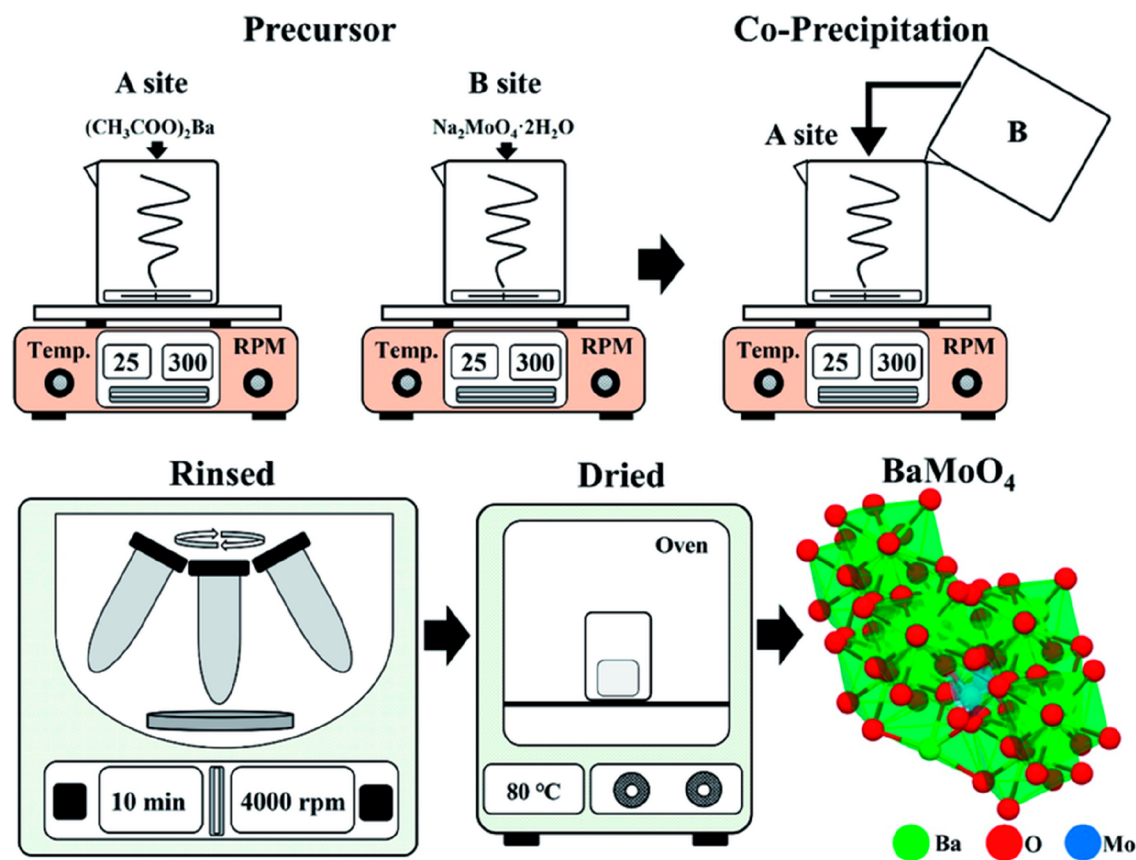


Figure 4. Schematic representation of the synthesis of BaMoO_4 through the coprecipitation method.⁸¹ Reprinted with permission from ref 81. Copyright 2022 Royal Society of Chemistry.

solutions were combined in a single platform and stirred continuously at 50 °C for 30 min. Immediately, NaOH solution was introduced slowly into the mixture until the pH of the solution got to 13.0. The combined solution of the precursors was stirred continuously until the creation of a black precipitate as shown in Figure 4. The precipitate was collected and treated with distilled water several times to remove excess chlorides, and oven-dried at 50 °C. Consequently, the finished product was calcined for 6 h at 800 °C. Usually, the liquid-state technique at very low temperatures is used to form nanoparticles from perovskite materials. However, submicron-sized perovskite materials can be created by burning them at a higher temperature, similar to the solid-state technique.⁸⁰

3.3. Gas-State Synthesis Technique. The gas-state synthesis technique is a bottom-up method for synthesizing multifunctional nanoparticles.⁸² The gas-state synthesis method uses a variety of processes, including lasers, furnaces, flames, and plasmas, to synthesize powdered oxide materials. Although their reactors are different, the fundamentals of thermodynamics and kinetics of the reaction are highly similar.⁶² The method of bottom-up nanofabrication is based on gathering nanomaterials from smaller components.⁶² These methods provide a fine dispersal of the nanoparticles. The dispersion must be reduced for the narrow distribution of the nanoparticles as it increases in the particle size.⁸³ Coevaporation of Y, Cu, and BaF_2 was used to create $\text{YBa}_2\text{Cu}_3\text{O}_7$ films, which were subsequently annealed at high temperatures in a moist O_2 environment with water vapor to speed up the annealing process and minimize substrate contact.⁶⁴

There are various techniques for the preparation of thin films, such as chemical vapor deposition, molecular beam epitaxy, laser ablation, direct current (DC) sputtering, magnetron sputtering, thermal evaporation, and electron beam evaporation.^{62,84,85} These methods are entirely distinct from other synthesis methods and are used to generate thin films for various electronic gadgets and solar cells made of perovskite materials.⁸⁶ For these synthesis techniques to provide the appropriate properties in the generated perovskite materials, an exact setup for high-quality samples is required.⁸⁷ Gas-state synthesis techniques are divided into three groups, namely; synthesis at the temperature of crystallization in an appropriate environment, fabrication at a temperature between 500 and 800 °C, followed by a postannealing process at a higher temperature, and fabrication with the substrate heated to a very high temperature afterward for postannealing.^{43,64,87}

The perovskite materials can be produced utilizing gas-state processes for a range of purposes, including photocatalysts, solar cells, optical and anticorrosion coatings, capacitor dielectrics, semiconductor devices, bioimplantable devices, chemical reactors, and catalysts.^{43,62} In the approaching years, industrial interest will undoubtedly rise in creating nanomaterial-based technologies through gas-state synthesis.⁸⁸

3.4. Electrospinning Method. Electrospinning is a widely used technique for the synthesis of perovskite oxide nanofibers. This approach offers a promising way to tailor the properties and applications of perovskite oxides. These oxides, which have an ABX_3 crystal structure, have gained significant attention due to their diverse functionalities, including catalysis, sensing, energy storage, and electronic devices.⁸⁹

To employ electrospinning for perovskite oxide synthesis, a precursor solution containing the metal cations (A and B-site elements) and the oxygen source required for perovskite oxide synthesis is prepared. The compatibility of the electrospinning process with the precursor salt and solvent should be considered while preparing the solution. The precursor solution is then loaded into a syringe equipped with a fine needle or spinneret, which is connected to the high-voltage power supply. A high voltage is applied to the precursor solution using the power supply, inducing electrostatic forces that draw the solution from the syringe tip toward the grounded collector. As the solution travels through the air, solvent evaporation occurs, leading to the formation of perovskite oxide nanofibers.^{90,91}

Following the electrospinning process, the as-spun perovskite oxide nanofibers are typically subjected to thermal treatment or annealing at elevated temperatures. This process is crucial for the crystallization of the perovskite structure and the removal of residual solvents, resulting in well-defined oxide nanofibers. By using electrospinning for perovskite oxide synthesis, researchers can achieve precise control over the morphology, structure, and properties of oxide nanofibers. This approach enables the development of advanced materials with tailored functionalities and applications. Moreover, the scalability and versatility of the electrospinning technique make it a promising approach for large-scale production of perovskite oxide nanofibers for various industrial and technological applications.^{92,93} Table 1 shows the merits and demerits of various routes of perovskite oxide, with respect to the conditions required to optimize them.

4. ELECTROCATALYTIC REDUCTION OF NITRATES BY PEROVSKITES

Conventional physicochemical technologies comprising biochemical treatment, ion exchange, and electrodialysis have been employed for nitrate reduction.⁹⁴ However, these technologies are confronted with certain drawbacks, including harsh operating environments, brine wastes after ion exchange, and the pretreatment requirements for electrodialysis. These limitations have hindered the large-scale applications of these technologies.⁹⁵ In contrast, the minimal input of chemicals, moderate operating conditions, and high efficiency of electrochemical reduction have made it a promising method over the aforementioned technologies. The electrocatalytic reduction of nitrate is a cost-effective and environmentally friendly method because the nitrate undergoes reduction by protonated hydrogen or electrons without using other reducing agents.⁹⁴ Studies have shown that electrocatalysis has excellent potential for removing nitrate. It offers the relative advantages of easy operation and simplicity of reactor structure.^{96,97}

The efficiency of electrocatalytic reduction can be improved by adjusting the parameters as well as the appropriate selection of suitable electrode materials. A suitable electrode material should be characterized by good corrosion resistance, high stability, high catalytic activity, and low cost.^{98,99} In many studies, metal cathode materials such as Pd, Pt, Cu, Co, Fe, Ni, and Ti have been developed to efficiently reduce nitrate.^{100–109} However, the use of these metal cathode materials is impaired by drawbacks owing to high toxicity and high cost.⁹⁹

Due to their low cost, flexible structure, and remarkable catalytic activity, perovskite materials have been thoroughly studied as alternatives to noble metal-based electrocatalysts.¹¹⁰ They are essential to the effort to achieve a sustainable energy

future. Numerous important reactions, including the reduction of oxygen, the evolution of oxygen, and the evolution of hydrogen, are catalyzed by these materials in electrocatalysis.¹¹¹ For instance, to ensure the sustainable synthesis of ammonia via the electrochemical reduction of nitrate, a study employed the use of bismuth ferrite (BiFeO₃) as an electrocatalyst.¹¹² The study demonstrated that deformed perovskite-type bismuth ferrite (BiFeO₃) flakes are excellent catalysts for the electrochemical production of NH₃ via nitrate reduction. At a voltage of -0.6 V versus the reversible hydrogen electrode, they achieved an NH₃ yield of 90.5 mg·h⁻¹·mg_{cat}⁻¹ and a maximum Faradaic efficiency of 96.9%.¹¹² The design and optimization of perovskite-based catalysts through ongoing research and development will propel substantial advancements in sustainable nitrate reduction technology. These developments could lead to more effective and environmentally friendly cleanup techniques.

Metal-modified biochar with advantageous physical and chemical surface characteristics has demonstrated great potential in the adsorption of water contaminants, including phosphate and nitrate. This is principally accomplished by interactions with the oxygen-containing functional groups on the surfaces of the biochar and/or ion exchange mechanisms. Metal-modified biochar may be promising in the electrocatalytic reduction of nitrate.¹¹³ This led Liu and his colleagues to adopt a typical perovskite/biochar nanocomposite, LaFeO₃/biochar, as a photocatalyst in a study owing to its strong magnetism, narrow band gap, and high stability.¹¹⁴ By copolymerizing Lotus biomass and Fe/La salts, composites of LaFeO₃ and biochar-rich in defective oxygen and surface functional groups were successfully produced. There was no usage of organic reagents during this process, which could have been hazardous to the environment. The subsequent photocatalytic reduction of nitrate to ammonia was carried out using the resultant nanocomposites. The study results in changed structural and surface characteristics of the catalysts through interactions with lanthanum (La³⁺) and iron (Fe³⁺) ions. The oxygen defects in LaFeO₃ were enhanced by adding biomass, hastening the electron–hole pair separation process. Simultaneously, Fe/La salts contributed to the surface alteration of the biochar during the carbonization process, increasing the exposure of aromatic structures and functional groups that contain oxygen, which promoted nitrate adsorption. Crucially, the REDOX-active quinone/phenol groups on the surface of the biochar promoted the selectivity of ammonium ion (NH₄⁺) as a direct electron donor by helping with the exchange of photogenerated electrons. Using the LaFeO₃/biochar photocatalyst under visible light irradiation, nitrate conversion reached 98%, and ammonia selectivity reached 97% when the mass ratio of lotus and Fe/La salts was optimized.¹¹⁴ An innovative method for reducing nitrate is to combine metal-modified biochar with perovskite-based nanocomposites. By utilizing the unique qualities of both materials, this synergistic combination improves catalytic performance and environmental sustainability. Such composite materials have a great deal of potential for cost-effective and scalable nitrate remediation, particularly in decentralized or resource-constrained environments where traditional treatment methods would not be practical.

Also, a highly effective catalyst is essential to achieving high conversion and selectivity in the electrochemical reduction of nitrate. The high activity of these catalysts allows them to accelerate the electrochemical reduction reaction, increasing

Table 1. Advantages and Disadvantages of Different Synthesis Routes of Perovskite Oxide

synthesis route	advantages	disadvantages
sol-gel method	<ul style="list-style-type: none"> • It is reproducible. • The reaction is simple and easy. • The sol-gel process allows precise control over the composition of the perovskite oxide by adjusting the precursor concentrations and ratios. This enables the synthesis of complex compositions and doping with various elements to tailor the properties of the materials. • The sol-gel method typically results in homogeneous mixtures at the molecular level, leading to a uniform distribution of components within the final perovskite oxide material. This uniformity enhances the material's properties and performance. • By adjusting parameters such as solvent type, pH, and drying conditions, the sol-gel method enables control over the morphology and microstructure of the perovskite oxide, which is crucial for optimizing its performance in different applications. • It is simple and cost-effective. • The combustion process can result in highly homogeneous materials with fine particle sizes and uniform distribution, leading to improved properties and performance of perovskite oxides. • This method can yield high-purity materials because the combustion process can effectively remove impurities through the formation of gaseous products. • Autocombustion synthesis offers good control over the stoichiometry of the synthesized perovskite oxide, leading to precise tuning of material properties. 	<ul style="list-style-type: none"> • Some precursor materials used in the sol-gel method may exhibit poor stability or reactivity, leading to difficulties in controlling the synthesis process and obtaining the desired perovskite oxide structure. • While the sol-gel method is suitable for laboratory-scale synthesis, scaling up production for industrial applications may be challenging due to issues such as reproducibility, uniformity, and cost-effectiveness. • The sol-gel process often requires prolonged heating or annealing steps, leading to higher energy consumption compared to some other synthesis methods. This can increase production costs and environmental impact. • Autocombustion synthesis may not be easily scalable for large-scale production due to the inherent limitations of the combustion process and the need for careful control over reaction conditions. • The combustion process involves complex chemical reactions, which can lead to challenges in controlling the reaction kinetics and product formation, potentially resulting in nonuniform or undesirable material properties. • Autocombustion synthesis involves combustion reactions, which can be hazardous if proper safety precautions are not followed, particularly due to the release of flammable gases and potential for uncontrolled reactions. • This method may not be suitable for synthesizing certain types of perovskite oxides or achieving specific material structures or morphologies, depending on the precursor chemistry and reaction conditions. • The as-synthesized materials may require additional processing steps, such as calcination or annealing, to improve crystallinity, phase purity, or other material properties, adding complexity to the overall synthesis process.
autocombustion method	<ul style="list-style-type: none"> • Electrospinning enables precise control over the morphology of perovskite oxide materials, allowing for the fabrication of nanofibers, nanotubes, or other nanostructures with high aspect ratios and specific surface areas. • The electrospinning process can produce highly uniform and continuous nanofibers, leading to enhanced material properties and performance compared to bulk counterparts. • Electrospinning can be combined with various precursor materials, dopants, and processing parameters to tailor the composition, structure, and properties of perovskite oxide nanofibers for specific applications. • The nanofibrous structure produced by electrospinning results in a high surface area-to-volume ratio, which is beneficial for applications such as catalysis, sensing, and energy storage. • Electrospinning is a scalable and relatively straightforward technique, making it suitable for large-scale production of perovskite oxide nanofibers compared to other synthesis methods. • Ball milling can achieve high efficiency in the synthesis of perovskite oxides by promoting rapid mixing and reaction between the precursor materials due to the intense mechanical forces generated during milling. • Ball milling ensures uniform mixing of precursor powders, leading to homogeneous distribution of components and improved stoichiometry control in the synthesized perovskite oxide materials. • Ball milling can reduce the particle size of perovskite oxide precursors to the nanoscale, resulting in increased surface area and enhanced reactivity, which is beneficial for achieving desired material properties. • Ball milling can be applied to various types of perovskite oxide precursors, including oxides, carbonates, and nitrates, allowing for the synthesis of a wide range of perovskite oxide compositions and structures. 	<ul style="list-style-type: none"> • It produces nanofibers with limited thickness, which may restrict the application of perovskite oxide nanofibers in certain contexts where thicker structures are required. • Achieving optimal electrospinning conditions for synthesizing perovskite oxide nanofibers can be challenging and often requires careful optimization of parameters such as solution viscosity, flow rate, applied voltage, and collector configuration. • Perovskite oxide nanofibers synthesized via electrospinning may require additional post-treatment steps, such as calcination or sintering, to enhance crystallinity, phase purity, and material properties, adding complexity to the synthesis process. • Electrospinning typically results in randomly oriented nanofibers, which may limit control over the alignment and orientation of perovskite oxide nanofibers, particularly for applications requiring specific structural arrangements. • Electrospinning setups can involve complex equipment and instrumentation, including high-voltage power supplies, syringe pumps, and specialized collectors, which may require expertise and investment in infrastructure for implementation and operation. • Ball milling requires high energy input due to the intense mechanical forces involved in the process, which can lead to increased energy consumption and equipment wear, particularly for prolonged milling durations or hard precursor materials. • Ball milling can introduce contaminants from the milling media (e.g., balls and vials) or atmosphere (e.g., oxygen, moisture) into the synthesized perovskite oxide materials, affecting their purity, phase composition, and properties. • Ball milling may result in nonequilibrium phases or crystal defects in the synthesized perovskite oxide materials, limiting control over crystal structure and potentially affecting material performance. • Ball milling can generate heat during the milling process, which may lead to temperature rise in the milling vial and the synthesized perovskite oxide materials, affecting reaction kinetics, phase formation, and material properties.
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Table 1. continued

synthesis route	advantages	disadvantages
coprecipitation method	<ul style="list-style-type: none"> • Ball milling is a scalable process suitable for both laboratory-scale research and large-scale production of perovskite oxide materials, making it a versatile and widely applicable synthesis technique. • Coprecipitation is a relatively simple and cost-effective method for synthesizing perovskite oxides compared to other techniques, requiring minimal equipment, and operating under mild conditions. • Coprecipitation typically yields perovskite oxide powders with high purity because the precipitation process effectively removes impurities through the formation of insoluble precipitates. • Coprecipitation allows for precise control over the stoichiometry of the synthesized perovskite oxide by adjusting the ratio of precursor salts in the solution, leading to tunable material properties. • Coprecipitation can produce highly homogeneous perovskite oxide powders with fine particle sizes and uniform distribution of components, resulting in improved material properties and performance. • Coprecipitation is easily scalable for large-scale production of perovskite oxide powders, making it suitable for industrial applications 	<ul style="list-style-type: none"> • Ball milling can cause particle agglomeration due to the adhesive forces between particles, leading to the nonuniform distribution of components and reduced effectiveness in achieving desired material properties. • Coprecipitation reactions can be relatively slow, requiring long reaction times to complete the precipitation process and achieve the desired phase formation and crystallinity in the synthesized perovskite oxide. • Coprecipitation may result in particle agglomeration or the formation of large aggregates due to the presence of high surface energy and the tendency of particles to coalesce during drying and calcination. • Coprecipitation often produces perovskite oxide powders with irregular shapes and sizes, limiting control over the morphology and surface properties of the synthesized materials compared to other synthesis methods. • The as-precipitated perovskite oxide powders may require additional processing steps, such as calcination or annealing, to improve crystallinity, phase purity, and material properties, adding complexity to the synthesis process. • Coprecipitation reactions are sensitive to reaction conditions such as temperature, pH, and stirring rate, which may require careful optimization to achieve reproducible results and desired material properties

the rate at which nitrate is converted into the desired product.¹¹⁵ Additionally, they exhibit excellent selectivity, which minimizes the production of undesirable byproducts while directing the reaction toward the intended product.¹¹⁵ These effective catalysts reduce overpotentials, suggesting that the reaction needs less energy. This improves the process's energy efficiency, which is important for industrial applications. The sustainability of the process is equally enhanced while reducing its environmental impact.^{116,117} This probably inspired the work of some researchers who assembled a perovskite (LaFeO₃) on hydrothermal carbonation carbon (HTCC) to obtain a nanostructured photocatalyst that was used for the reduction of nitrate to ammonia.¹¹⁸ The two-dimensional HTCC nanosheet has several surface functional groups and a substantial specific surface area. Fe/La salt was used to modify the surface of HTCC, increasing the aromatic structure and the exposure of oxygen-containing functional groups and promoting nitrate adsorption. Furthermore, a p–n heterojunction between HTCC and LaFeO₃ was created, facilitating the quick separation of photogenerated electron holes and improving photocatalytic activity. Under the effect of visible light irradiation, the LaFeO₃/HTCC photocatalyst obtained a peak nitrate removal of 94.6% and an ammonia selectivity of 88.7% when the mass ratios of pomegranate peel to Fe/La salt were optimized.¹¹⁸

While the catalytic activities and tunable physicochemical properties of perovskites have made them resourceful in the reduction of nitrates, their design strategies have been predominantly focused on the selection of B-site cations to enhance the reduction process through the mechanisms of Mars-van-Krevelen-like, Langmuir–Hinshelwood-like, or Eley–Rideal pathways which usually proceed on metal sites.^{119–121} However, recent observations have shown that modification strategies can be employed to improve the efficiency of electrocatalytic nitrate reduction. One such strategy involves doping metal cation on the B-site of perovskite, which was adopted in a study by Zhang and his Colleagues.¹²² The study employed the doping of Mn cation on the B-site of LaCoO₃ and investigated its performance in the electrochemical reduction of nitrate. LaMn_{0.6}Co_{0.4}O₃, the optimized doped material, showed a nitrate removal efficiency of 41.9%, greater than LaCoO₃. The study reported that the doped material exhibited outstanding stability after 10 consecutive reaction cycles and performed well under various operating conditions, such as pH levels, cathode potentials, and varying initial nitrate concentrations. It was deduced that the doped Mn cation not only affected the valence of the Co cation but also activated adsorbed oxygen to give an electron and speed up electron transfer based on the observed changes in the valence of Co and Mn in the cathode before and after electrocatalysis.¹²²

Furthermore, it has been suggested that the activity of perovskite is widely influenced by the electronic environment around the active sites.¹²³ Perovskite oxides exhibit a remarkable degree of compositional flexibility since they can accommodate about 90% of the metallic elements found in the periodic table. As a result, metal elements can be integrated to produce a bimetallic perovskite at the B-site. The catalytic performance of these perovskite oxides can be altered based on band theory and molecular orbital theory. This can be accomplished by modifying their [BO₆] units' octahedral structure, managing the hybridization of B–O bonds, and generating oxygen vacancies. For example, it has been

established that a critical component of electrocatalytic activity is the covalency of the bonds between transition metals and oxygen, which reflects the adsorption strength of intermediates connected to oxygen.^{124,125} In this regard, Chu and his Colleagues attempted to optimize the adsorption strength of intermediates by constructing a series of Fe-rich perovskite oxides of $\text{LaFe}_{0.9}\text{M}_{0.1}\text{O}_{3-\delta}$ (where M = Cu, Ni, and Co) from the starting material $\text{LaFeO}_{3-\delta}$ (LF) by a B-site substitution strategy.¹²⁶ The results of the study showed that the $\text{LaFe}_{0.9}\text{Cu}_{0.1}\text{O}_{3-\delta}$ ($\text{LF}_{0.9}\text{Cu}_{0.1}$) submicrofibers showed a superior ammonia yield rate of $349 \pm 15 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$, and a Faradaic efficiency of $48 \pm 2\%$, compared to LF submicron fibers. These submicrofibers have a more robust Fe–O hybridization, an increased number of oxygen vacancies, and a more positive surface potential.¹²⁶

Moreover, oxygen vacancies have been reported to enhance the selectivity and efficiency of the electrochemical reduction of nitrate. The N–O bond in nitrate can be efficiently activated by oxygen vacancies, which improves the yield and selectivity of the nitrate reduction process to ammonia.¹²⁷ Also, by modifying the local electronegativity and coordination environment, oxygen vacancies added to the structure of catalysts for oxygenated compounds can enhance the catalytic property of the nitrogen reduction process.¹²⁸ Hence, an attempt to improve the performance of electrochemical nitrate reduction could incorporate the engineering of oxygen vacancies. It traps metastable electrons in the antibonding orbitals of nitrogen molecules, breaking the $\text{N}\equiv\text{N}$ bond and facilitating fast electron transport.¹²⁹ In a study by Feng et al.,¹² NbWO_6 perovskite nanosheets with oxygen vacancy were investigated in the selective electro-reduction of nitrate. In this study, thermal treatment and exfoliation were used to create NbWO_6 nanosheets with an oxygen vacancy (NbWO_{6-x}), which showed an NH_3 selectivity of 86.8% and a Faradaic efficiency of 85.7% toward the electrocatalytic reduction of nitrate. Using ^1H nuclear magnetic resonance spectra and ^{15}N isotope labeling tests, the origin of NH_3 from NO_3^- was verified. Computational studies were conducted to reveal the role of the oxygen vacancy in the electrocatalytic reduction of nitrate.¹² Similarly, another study by Yang and his colleagues aimed to improve the performance of perovskite oxides by oxygen vacancies engineering.¹³⁰ The study presented a novel and effective electrochemical activation technique for the in situ synthesis of oxygen vacancies (OVs). The results showed that the activated $\text{La}_{0.9}\text{FeO}_{3-\delta}$ had a NO_3^- -N removal rate that was 2.6 times higher than the unmodified $\text{La}_{0.9}\text{FeO}_{3-\delta}$. The greater adsorption energy of NO_3^- and the facilitation of the synthesis of atomic hydrogen (H^*) for the hydrogenation of NO_3^- -N were credited to the increased presence of OVs, which also improved the performance of the nitrate reduction reaction. Furthermore, a 240 h continuous experiment showed that the activated $\text{La}_{0.9}\text{FeO}_{3-\delta}$ remained exceptionally stable.¹³⁰ In addition, the electrochemical reduction of nitrate can be improved by A-site deficiency engineering of the electrocatalysts. This was reflected in a study by Liu and colleagues.¹¹⁰ The study presented a practical method for modifying the A-site deficiencies in cobalt-based perovskite oxides to increase nitrate electro-reduction activity (NO_3ER). To demonstrate the concept, the authors used a sequence of $(\text{Ba}_{0.5}\text{Sr}_{0.5})_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, where $x = 0, 0.05, 0.10, 0.15,$ and 0.20 . Their NO_3ER activity peaked at $x = 0.15$ and showed a volcano-type reliance on the x values. To be more precise, $(\text{BS})_{0.85}\text{CF}$ outperformed most previously reported NO_3ER

catalysts in terms of activity ($143 \text{ mg}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$ or $0.86 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$), selectivity (97.9%), and stability (200 h) at -0.45 V (vs. RHE). The optimized properties of NO_3ER can be explained by the modulation of physicochemical properties caused by A-site inadequacies, including the introduction of a modest distance between the Fermi level and the band center and the production of a moderate amount of oxygen vacancies.¹¹⁰

The potential for improving the catalytic efficiency of perovskite oxides in nitrate reduction is highlighted by the application of modification techniques such as metal doping and oxygen vacancy engineering. A more thorough comprehension of the fundamental mechanisms driving these modifications will make catalyst design more accurate and efficient.

Recently, the construction of perovskite oxides with sufficient active sites for the electrochemical reduction of nitrate has seemed to be challenging. This has brought about the adoption of high entropy materials. High entropy materials are particularly useful in electrocatalysis owing to random element distribution, complex electronic structures, and intrinsic abundant active sites.¹³¹ While various high entropy materials including phosphate, carbides, and nitrides have been developed, high entropy perovskites seem to be generating considerable interest due to their structural stability, several active sites, and tunable constituent elements.¹³² Chu and his colleagues investigated high-entropy perovskite oxides as electrocatalytic nitrogen reduction reaction (eNRR) catalysts. These oxides have the composition $\text{Ba}_x(\text{FeCoNiZrY})_{0.2}\text{O}_{3-\delta}$, where $x = 0.9$ and 1 . The materials produced more oxygen vacancies at the A-site by changing the non stoichiometric metal components. Particularly, high-entropy perovskite oxides exhibited a markedly increased eNRR activity. Specifically, compared to $\text{B}(\text{FCNZY})_{0.2}$, the NH_3 yield and Faraday efficiency for $\text{B}_{0.9}(\text{FCNZY})_{0.2}$ were 1.95 and 1.51 times greater, respectively.¹³¹ This underscores the importance of designing and developing novel high entropy perovskite oxides with advanced microstructures that will simultaneously accelerate the reactions as well as increase the number of active sites on the perovskite oxides.

Because of their high conductivity and stability, transition metal oxides have found extensive use as electrocatalysts.¹³³ However, their Faradaic efficiency is frequently constrained, particularly in oxygen evolution reactions (OER). Unwanted byproducts may be produced during OER as a result of side reactions.¹³⁴ In contrast, perovskite oxides show better Faradaic efficiency in OER, as evident in the studies earlier reported. Their high surface area and adjustable electronic structure reduce side reactions and improve selectivity for the intended oxygen evolution process, which is why they are relatively superior to other materials. Perovskite oxides are attractive options for effective electrocatalysis because of these characteristics. In addition, the catalytic activity of noble metals, such as platinum (Pt) and gold (Au), in a variety of electrochemical reactions is widely recognized. Unfortunately, their high price and limited availability prevent them from being widely used.^{135,136} Furthermore, even though noble metals have a high Faradaic efficiency, they can deactivate and become poisonous in harsh operating conditions.^{137,138} Perovskite oxides offer an appealing alternative. In certain processes, such as oxygen reduction reactions (ORR), they provide similar or even better Faradaic efficiency. In addition, perovskite oxides are more resilient and prevalent than noble

metals. Their favorable cost-performance ratio makes them an attractive option for long-term electrocatalysis. Also, the high surface area and tunable features of carbon-based materials, such as graphene and carbon nanotubes, have attracted a lot of interest as electrocatalysts.¹³⁹ However, heterogeneous architectures and surface defects might reduce their Faradaic efficiencies, leading to unpredictable catalytic behavior.¹⁴⁰ Perovskite oxides, however, have surface chemistry that can be controlled and well-defined crystalline structures. They consequently show improved stability and increased Faradaic efficiency in a range of electrochemical processes. Perovskite oxides are potential options for dependable and effective electrocatalysis because of their characteristics. Finally, metal sulfides and selenides have become more and more popular as electrocatalysts owing to their abundance and advantageous catalytic characteristics.^{141,142} However, slow kinetics and unfavorable side effects have the potential to hinder their Faradaic efficiency.^{143,144} Perovskite oxides provide a higher Faradaic efficiency due to their unique electronic structure and composition. They do this by promoting charge transfer and reducing energy losses.^{145–147} Consequently, in a number of electrochemical processes, perovskite oxides perform better than metal sulfides and selenides.

The preceding studies highlighted several ways to modify perovskite materials to increase their electrocatalytic performance for nitrate reduction. These include the creation of oxygen vacancies, metal doping, and engineering of A-site deficiencies. Various approaches demonstrated how flexible perovskite structures are and how they may be tailored for specific catalytic applications. Most of the studies emphasized how perovskite-based electrocatalysts for nitrate reduction provide great catalytic efficiency and selectivity. Many studies highlighted the environmentally favorable features of synthesis methods, like using biomass to create perovskite-based catalysts and avoiding dangerous organic reagents. These factors highlighted the potential of perovskite electrocatalysts to support environmentally friendly activities and are consistent with the growing emphasis on green and sustainable chemistry. Nevertheless, despite the strong magnetism, narrow band gap, and great stability displayed by perovskites like LaFeO₃/biochar, further investigation is still required to determine their long-term stability under a range of operating conditions. The mass ratio of biomass to metal salts is one of the many variables that can impact the performance of perovskite/biochar composites. Meticulous adjustments are required for these parameters to function at their best. Even though research on a laboratory scale has produced promising results, it is still unclear whether these approaches can be scaled up to industrial levels.

5. FUTURE PERSPECTIVES AND CONCLUSIONS

In this review, we provided an overview of nitrates and their toxicity. Additionally, we discussed the use of perovskites and perovskite oxides for nitrate reduction. We looked at the electrocatalytic nitrate reduction mechanism, including surface modifications, metal doping, and the importance of oxygen vacancies. However, to develop better catalysts, we need a deeper understanding of their fundamental mechanisms, such as the exact pathways of the reduction events and how perovskite structures interact with nitrate ions. Perovskite oxides have shown high catalytic activity in nitrate reduction reactions, indicating their potential to remove nitrates from water sources effectively. Selectivity toward desired products is

crucial in nitrate reduction reactions to avoid the formation of harmful intermediates. Perovskite oxides usually have good selectivity toward nitrogen gas, which is a harmless end product. Stability of the catalysts over extended periods is essential for practical applications. Perovskite oxides have shown good stability under certain conditions, but further research is necessary to optimize stability in different environments.

Although the reviewed studies' findings are promising, it is crucial to identify potential obstacles and areas that require further research. We must consider the catalyst's stability across multiple reaction cycles, its scalability for industrial use, and the toxicity of specific metal ions. Additionally, more research is necessary to determine the durability and long-term performance of perovskite-based electrocatalysts in real-world applications. In the future, researchers could combine perovskite-based electrocatalysts with other technologies, such as advanced sensing and monitoring systems, to increase the overall efficiency of nitrate reduction processes. This would provide real-time feedback and control, maximizing the efficiency of reaction conditions while minimizing the generation of undesirable byproducts.

To implement perovskite oxides for nitrate reduction in real-world situations, we must evaluate their economic feasibility and scalability. Factors such as the availability of raw materials, synthesis costs, and scalability of production methods must be considered. We must also assess the overall environmental impact of using perovskite oxides for nitrate reduction, including energy requirements for synthesis, potential by-products, and the process's overall sustainability. Integrating perovskite oxide-based catalysts into current water treatment systems or developing new systems is necessary to ensure practical applicability. In conclusion, although perovskite oxides show promise as catalysts for nitrate reduction, further research is necessary to address stability, scalability, cost-effectiveness, and environmental impact challenges before widespread implementation. Collaborative efforts between researchers, industry, and policymakers are essential to realize the full potential of perovskite oxide-based catalysis for nitrate reduction and effectively mitigate nitrate pollution.

■ AUTHOR INFORMATION

Corresponding Authors

Martins O. Omorogie – Department of Chemical Sciences, Faculty of Natural Sciences, Redeemer's University, 232101 Ede, Nigeria; Environmental Science and Technology Unit, African Centre of Excellence for Water and Environmental Research (ACEWATER), Redeemer's University, 232101 Ede, Nigeria; Chair of Urban Water Systems Engineering, School of Engineering and Design, Technical University of Munich (TUM), 85748 Garching, Germany; orcid.org/0000-0001-9697-2960; Email: mo.omorogie@tum.de, omorogie@run.edu.ng, dromorogiemoon@gmail.com

Ajibola A. Bayode – College of Chemical Engineering, Sichuan University of Science and Engineering, Zigong 643000, P. R. China; Department of Chemical Sciences, Faculty of Natural Sciences, Redeemer's University, 232101 Ede, Nigeria; orcid.org/0000-0003-2461-6208; Email: bayodea@run.edu.ng, ajibolabay7@gmail.com

Authors

Oduwayo T. Ore – Department of Chemical Sciences, Achiever's University, 341101 Owo, Nigeria

Esther A. Nnamani – Department of Chemical Sciences, Faculty of Natural Sciences, Redeemer's University, 232101 Ede, Nigeria; Environmental Science and Technology Unit, African Centre of Excellence for Water and Environmental Research (ACEWATER), Redeemer's University, 232101 Ede, Nigeria

Babajide Sotunde – Department of Chemical Sciences, Faculty of Natural Sciences, Redeemer's University, 232101 Ede, Nigeria; Environmental Science and Technology Unit, African Centre of Excellence for Water and Environmental Research (ACEWATER), Redeemer's University, 232101 Ede, Nigeria

Daniel T. Koko – Department of Chemical Sciences, Faculty of Natural Sciences, Redeemer's University, 232101 Ede, Nigeria; Environmental Science and Technology Unit, African Centre of Excellence for Water and Environmental Research (ACEWATER), Redeemer's University, 232101 Ede, Nigeria

Emmanuel I. Unuabonah – Department of Chemical Sciences, Faculty of Natural Sciences, Redeemer's University, 232101 Ede, Nigeria; Environmental Science and Technology Unit, African Centre of Excellence for Water and Environmental Research (ACEWATER), Redeemer's University, 232101 Ede, Nigeria

Brigitte Helmreich – Chair of Urban Water Systems Engineering, School of Engineering and Design, Technical University of Munich (TUM), 85748 Garching, Germany; orcid.org/0000-0003-4224-3329

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.4c01487>

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Dou, J.; Xu, M.; Tan, B.; Lu, X.; Mo, H.; Wang, B.; Liu, N. Research Progress of Nitrate Ester Binders. *FirePhysChem.* **2023**, *3*, 54.
- (2) Singh, S.; Anil, A. G.; Kumar, V.; Kapoor, D.; Subramanian, S.; Singh, J.; Ramamurthy, P. C. Nitrates in the environment: A critical review of their distribution, sensing techniques, ecological effects and remediation. *Chemosphere* **2022**, *287*, 131996.
- (3) Ahluwalia, A.; Gladwin, M.; Coleman, G. D.; Hord, N.; Howard, G.; Kim-Shapiro, D. B.; Lajous, M.; Larsen, F. J.; Lefter, D. J.; McClure, L. A.; Nolan, B. T.; Pluta, R.; Schechter, A.; Wang, C. Y.; Ward, M. H.; Harman, J. L. Dietary Nitrate and the Epidemiology of Cardiovascular Disease: Report From a National Heart, Lung, and Blood Institute Workshop. *J. Am. Heart Assoc.* **2016**, *5*, No. e003402.
- (4) Yang, W.-J.; Yang, L.-H.; Peng, H.-J.; Lv, S.-H.; Muhammad Adeel Sharif, H.; Sun, W.; Li, W.; Yang, C.; Lin, H. Perovskite oxide LaMO_{3-δ} (M = Fe, Co, Ni and Cu) cathode for efficient electroreduction of nitrate. *Sep. Purif. Technol.* **2022**, *295*, 121278.
- (5) Ma, L.; Hu, L.; Feng, X.; Wang, S. Nitrate and Nitrite in Health and Disease. *Aging Dis* **2018**, *9*, 938–945.
- (6) Tyagi, S.; Rawtani, D.; Khatri, N.; Tharmavaram, M. Strategies for Nitrate removal from aqueous environment using Nano-

technology: A Review. *Journal of Water Process Engineering* **2018**, *21*, 84–95.

(7) Thompson, T. S. Nitrate concentrations in private rural drinking water supplies in Saskatchewan, Canada. *Bull. Environ. Contam. Toxicol.* **2001**, *66*, 64–70.

(8) Dahan, O.; Babad, A.; Lazarovitch, N.; Russak, E.; Kurtzman, D. Nitrate leaching from intensive organic farms to groundwater. *Hydrol. Earth Syst. Sci.* **2014**, *18*, 333.

(9) Ahada, C. P. S.; Suthar, S. Groundwater nitrate contamination and associated human health risk assessment in southern districts of Punjab, India. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 25336–25347.

(10) Li, F.; Zhang, P.; Zhang, W.; Fang, D.; Li, K. Activity trend and possible descriptor of LaBO₃ (B = Cr, Mn, Fe, Co) perovskite catalysts for electroreduction of nitrate. *Chemical Engineering Journal* **2023**, *472*, 145148.

(11) Schaidler, L. A.; Swetschinski, L.; Campbell, C.; Rudel, R. A. Environmental justice and drinking water quality: are there socio-economic disparities in nitrate levels in U.S. drinking water? *Environ. Health* **2019**, *18*, 3.

(12) Feng, T.; Li, F.; Hu, X.; Wang, Y. Selective electroreduction of nitrate to ammonia via NbWO₆ perovskite nanosheets with oxygen vacancy. *Chin. Chem. Lett.* **2023**, *34*, 107862.

(13) Anjana, A.; Umar, S.; Iqbal, M. Nitrate accumulation in plants, factors affecting the process, and human health implications. A review. *Agron. Sustainable Dev.* **2007**, *27*, 45–57.

(14) Lee, C.; Beauchemin, K. A review of feeding supplementary nitrate to ruminant animals: Nitrate toxicity, methane emissions, and production performance. *Canadian Journal of Animal Science* **2014**, *94*, 557–570.

(15) Quist, A. J. L.; Inoue-Choi, M.; Weyer, P. J.; Anderson, K. E.; Cantor, K. P.; Krasner, S.; Freeman, L. E. B.; Ward, M. H.; Jones, R. R. Ingested nitrate and nitrite, disinfection by-products, and pancreatic cancer risk in postmenopausal women. *Int. J. Cancer* **2018**, *142*, 251–261.

(16) Jones, R. R.; Weyer, P. J.; DellaValle, C. T.; Inoue-Choi, M.; Anderson, K. E.; Cantor, K. P.; Krasner, S.; Robien, K.; Freeman, L. E.; Silverman, D. T.; Ward, M. H. Nitrate from Drinking Water and Diet and Bladder Cancer Among Postmenopausal Women in Iowa. *Environ. Health Perspect* **2016**, *124*, 1751–1758.

(17) Ferrucci, L. M.; Sinha, R.; Ward, M. H.; Graubard, B. I.; Hollenbeck, A. R.; Kilfoy, B. A.; Schatzkin, A.; Michaud, D. S.; Cross, A. J. Meat and components of meat and the risk of bladder cancer in the NIH-AARP Diet and Health Study. *Cancer* **2010**, *116*, 4345–4353.

(18) Inoue-Choi, M.; Sinha, R.; Gierach, G. L.; Ward, M. H. Red and processed meat, nitrite, and heme iron intakes and postmenopausal breast cancer risk in the NIH-AARP Diet and Health Study. *Int. J. Cancer* **2016**, *138*, 1609–1618.

(19) Inoue-Choi, M.; Jones, R. R.; Anderson, K. E.; Cantor, K. P.; Cerhan, J. R.; Krasner, S.; Robien, K.; Weyer, P. J.; Ward, M. H. Nitrate and nitrite ingestion and risk of ovarian cancer among postmenopausal women in Iowa. *Int. J. Cancer* **2015**, *137*, 173–182.

(20) Ward, M. H.; Jones, R. R.; Brender, J. D.; de Kok, T. M.; Weyer, P. J.; Nolan, B. T.; Villanueva, C. M.; van Breda, S. G. Drinking Water Nitrate and Human Health: An Updated Review. *Int. J. Environ. Res. Public Health* **2018**, *15*, 1557.

(21) López-Suárez, F. E.; Illán-Gómez, M. J.; Bueno-López, A.; Anderson, J. A. NO_x storage and reduction on a SrTiCuO₃ perovskite catalyst studied by operando DRIFTS. *Applied Catalysis B: Environmental* **2011**, *104*, 261–267.

(22) Zhu, I.; Getting, T. A review of nitrate reduction using inorganic materials. *Environmental Technology Reviews* **2012**, *1*, 46–58.

(23) Akinnawo, S. O. Eutrophication: Causes, consequences, physical, chemical and biological techniques for mitigation strategies. *Environmental Challenges* **2023**, *12*, 100733.

(24) Salbitani, G.; Carfagna, S. Ammonium utilization in microalgae: A sustainable method for wastewater treatment. *Sustainability* **2021**, *13*, 956.

- (25) Rosier, B. T.; Takahashi, N.; Zaura, E.; Krom, B. P.; Martínez-Espinosa, R. M.; van Breda, S. G.; Marsh, P. D.; Mira, A. The importance of nitrate reduction for oral health. *Journal of Dental Research* **2022**, *101*, 887–897.
- (26) Liang, J.; Liu, Q.; Alshehri, A. A.; Sun, X. Recent advances in nanostructured heterogeneous catalysts for N-cycle electrocatalysis. *Nano Res. Energy* **2022**, *1*, e9120010.
- (27) Zhang, H.; Wang, C.; Luo, H.; Chen, J.; Kuang, M.; Yang, J. Iron nanoparticles protected by chainmail-structured graphene for durable electrocatalytic nitrate reduction to nitrogen. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202217071.
- (28) Chen, H.; Zeng, L.; Wang, D.; Zhou, Y.; Yang, X. Recent advances in nitrous oxide production and mitigation in wastewater treatment. *Water Res.* **2020**, *184*, 116168.
- (29) Theerthagiri, J.; Park, J.; Das, H. T.; Rahamathulla, N.; Cardoso, E. S.; Murthy, A. P.; Maia, G.; Vo, D. V. N.; Choi, M. Y. Electrocatalytic conversion of nitrate waste into ammonia: a review. *Environmental Chemistry Letters* **2022**, *20*, 2929–2949.
- (30) Oka, M.; Miseki, Y.; Saito, K.; Kudo, A. Photocatalytic reduction of nitrate ions to dinitrogen over layered perovskite BaLa₄Ti₄O₁₅ using water as an electron donor. *Applied Catalysis B: Environmental* **2015**, *179*, 407–411.
- (31) Wu, Z.; Song, Y.; Guo, H.; Xie, F.; Cong, Y.; Kuang, M.; Yang, J. Tandem catalysis in electrocatalytic nitrate reduction: Unlocking efficiency and mechanism. *Interdiscip. Mater.* **2024**, *3*, 245.
- (32) Song, W.; Yue, L.; Fan, X.; Luo, Y.; Ying, B.; Sun, S.; Zheng, D.; Liu, Q.; Hamdy, M. S.; Sun, X. Recent progress and strategies on design of catalysts for electrochemical ammonia synthesis from nitrate reduction. *Inorg. Chem. Front.* **2023**, *10*, 3489.
- (33) Fan, X.; Liu, C.; Li, Z.; Cai, Z.; Ouyang, L.; Li, Z.; He, X.; Luo, Y.; Zheng, D.; Sun, S.; Wang, Y.; Ying, B.; Liu, Q.; Farouk, A.; Hamdy, M. S.; Gong, F.; Sun, X.; Zheng, Y. Pd-Doped Co₃O₄ nanoarray for efficient eight-electron nitrate electrocatalytic reduction to ammonia synthesis. *Small* **2023**, *19*, 2303424.
- (34) Zhang, R.; Villanueva, A.; Alamdari, H.; Kaliaguine, S. Cu- and Pd-substituted nanoscale Fe-based perovskites for selective catalytic reduction of NO by propene. *J. Catal.* **2006**, *237*, 368–380.
- (35) Irshad, M.; Ain, Q. T.; Zaman, M.; Aslam, M. Z.; Kousar, N.; Asim, M.; Rafique, M.; Siraj, K.; Tabish, A. N.; Usman, M.; Hassan Farooq, M. U.; Assiri, M. A.; Imran, M. Photocatalysis and perovskite oxide-based materials: a remedy for a clean and sustainable future. *RSC Adv.* **2022**, *12*, 7009–7039.
- (36) Ortega-San-Martin, L.: 1 - Introduction to perovskites. In *Perovskite Ceramics*; Huamán, J. L. C., Rivera, V. A. G., Eds.; Elsevier: Amsterdam, **2023**; pp 3–29.
- (37) Darriet, J.; Subramanian, M. A. Structural relationships between compounds based on the stacking of mixed layers related to hexagonal perovskite-type structures. *J. Mater. Chem.* **1995**, *5*, 543–552.
- (38) Arandiyán, H.; Wang, Y.; Sun, H.; Rezaei, M.; Dai, H. Ordered meso- and macroporous perovskite oxide catalysts for emerging applications. *Chem. Commun.* **2018**, *54*, 6484–6502.
- (39) Arandiyán, H.; Wang, Y.; Sun, H.; Rezaei, M.; Dai, H. Ordered meso- and macroporous perovskite oxide catalysts for emerging applications. *Chem. Commun. (Camb)* **2018**, *54*, 6484–6502.
- (40) Bian, Z.; Kawi, S. Preparation, characterization and catalytic application of phyllosilicate: A review. *Catal. Today* **2020**, *339*, 3–23.
- (41) Zhu, J.; Li, H.; Zhong, L.; Xiao, P.; Xu, X.; Yang, X.; Zhao, Z.; Li, J. Perovskite Oxides: Preparation, Characterizations, and Applications in Heterogeneous Catalysis. *ACS Catal.* **2014**, *4*, 2917–2940.
- (42) Chen, Y.; Zhang, L.; Zhang, Y.; Gao, H.; Yan, H. Large-area perovskite solar cells – a review of recent progress and issues. *RSC Adv.* **2018**, *8*, 10489–10508.
- (43) Assirey, E. A. R. Perovskite synthesis, properties and their related biochemical and industrial application. *Saudi Pharm. J.* **2019**, *27*, 817–829.
- (44) Kubacka, A.; Fernandez-Garcia, M.; Colon, G. Advanced nanoarchitectures for solar photocatalytic applications. *Chem. Rev.* **2012**, *112*, 1555–1614.
- (45) Peña, M. A.; Fierro, J. L. Chemical structures and performance of perovskite oxides. *Chem. Rev.* **2001**, *101*, 1981–2018.
- (46) Huang, L.; Bassir, M.; Kaliaguine, S. Characters of perovskite-type LaCoO₃ prepared by reactive grinding. *Mater. Chem. Phys.* **2007**, *101*, 259–263.
- (47) Wang, Y.; Wu, T.; Barbaud, J.; Kong, W.; Cui, D.; Chen, H.; Yang, X.; Han, L. Stabilizing heterostructures of soft perovskite semiconductors. *Science* **2019**, *365* (6454), 687–691.
- (48) Malavasi, L.; Fisher, C. A. J.; Islam, M. S. Oxide-ion and proton conducting electrolyte materials for clean energy applications: structural and mechanistic features. *Chem. Soc. Rev.* **2010**, *39*, 4370–4387.
- (49) West, A. R.: Perovskite: A Solid-State Chemistry Chameleon, Illustrating the Elements, Their Properties and Location in the Periodic Table. In *The Periodic Table II: Catalytic, Materials, Biological and Medical Applications*; Mingos, D. M. P., Ed.; Springer International Publishing: Cham, **2019**; pp 121–152.
- (50) Moure, C.; Peña, O. Recent advances in perovskites: Processing and properties. *Prog. Solid State Chem.* **2015**, *43*, 123–148.
- (51) Marchand, R.; Laurent, Y.; Guyader, J.; L'Haridon, P.; Verdier, P. Nitrides and oxynitrides: Preparation, crystal chemistry and properties. *Journal of the European Ceramic Society* **1991**, *8*, 197–213.
- (52) Žužič, A.; Ressler, A.; Macan, J. Perovskite oxides as active materials in novel alternatives to well-known technologies: A review. *Ceram. Int.* **2022**, *48*, 27240–27261.
- (53) Bayode, A. A.; Emmanuel, S. S.; Osti, A.; Olorunnisola, C. G.; Egbiedina, A. O.; Koko, D. T.; Adedipe, D. T.; Helmreich, B.; Omorogie, M. O. Applications of perovskite oxides for the cleanup and mechanism of action of emerging contaminants/steroid hormones in water. *Journal of Water Process Engineering* **2024**, *58*, 104753.
- (54) Royer, S.; Duprez, D.; Can, F.; Courtois, X.; Batiot-Dupeyrat, C.; Laassiri, S.; Alamdari, H. Perovskites as Substitutes of Noble Metals for Heterogeneous Catalysis: Dream or Reality. *Chem. Rev.* **2014**, *114*, 10292–10368.
- (55) Hwang, J.; Feng, Z.; Charles, N.; Wang, X. R.; Lee, D.; Stoerzinger, K. A.; Mui, S.; Rao, R. R.; Lee, D.; Jacobs, R.; Morgan, D.; Shao-Horn, Y. Tuning perovskite oxides by strain: Electronic structure, properties, and functions in (electro)catalysis and ferroelectricity. *Mater. Today* **2019**, *31*, 100–118.
- (56) Peña, M. A.; Fierro, J. L. G. Chemical Structures and Performance of Perovskite Oxides. *Chem. Rev.* **2001**, *101*, 1981–2018.
- (57) Pankaj, P. K.; Anil, V. R.: Perovskite Structured Materials: Synthesis, Structure, Physical Properties and Applications. In *Recent Advances in Multifunctional Perovskite Materials*; Poorva, S., Ashwini, K., Eds.; IntechOpen: Rijeka, **2022**; Ch. 1.
- (58) Nkwachukwu, O. V.; Arotiba, O. A. Perovskite Oxide-Based Materials for Photocatalytic and Photoelectrocatalytic Treatment of Water. *Front Chem.* **2021**, *9*, 634630.
- (59) Arya, S.; Mahajan, P.; Gupta, R.; Srivastava, R.; Tailor, N. K.; Satapathi, S.; Sumathi, R. R.; Datt, R.; Gupta, V. A comprehensive review on synthesis and applications of single crystal perovskite halides. *Prog. Solid State Chem.* **2020**, *60*, 100286.
- (60) Zhang, M.; Jeerh, G.; Zou, P.; Lan, R.; Wang, M.; Wang, H.; Tao, S. Recent development of perovskite oxide-based electrocatalysts and their applications in low to intermediate temperature electrochemical devices. *Mater. Today* **2021**, *49*, 351–377.
- (61) Vidyasagar, C. C.; Munoz Flores, B. M.; Jimenez Perez, V. M. Recent Advances in Synthesis and Properties of Hybrid Halide Perovskites for Photovoltaics. *Nanomicro Lett.* **2018**, *10*, 68.
- (62) Dinesh, K.; Ram Sagar, Y.; Monika; Akhilesh Kumar, S.; Shyam Bahadur, R.: Synthesis Techniques and Applications of Perovskite Materials. In *Perovskite Materials, Devices and Integration*; He, T., Ed.; IntechOpen: Rijeka, **2020**; pp Ch. 3.
- (63) Zhang, H.; Sun, S.; Liu, W.; Ding, H.; Zhang, J. Synthesis of Perovskite by Solid-Phase Method with Metatitanic Acid and Calcium Carbonate and Its Pigment Properties Investigation. *Materials (Basel)* **2020**, *13*, 1508.

- (64) Nada, F. A.; Ahmed, G.; Ekram, H. E.-A.: Perovskite Nanomaterials – Synthesis, Characterization, and Applications. In *Perovskite Materials*; Likun, P., Guang, Z., Eds.; IntechOpen: Rijeka, 2016; pp Ch. 4.
- (65) Piotr, D.: Solid-State Mechanochemical Syntheses of Perovskites. In *Perovskite Materials*; Likun, P., Guang, Z., Eds.; IntechOpen: Rijeka, 2016; pp Ch. 1.
- (66) Zhang, L.; Xu, Z.; Cao, L.; Yao, X. Synthesis of BF–PT perovskite powders by high-energy ball milling. *Mater. Lett.* **2007**, *61*, 1130–1133.
- (67) Yan, J.; Li, H.; Aldamasy, M. H.; Frasca, C.; Abate, A.; Zhao, K.; Hu, Y. Advances in the Synthesis of Halide Perovskite Single Crystals for Optoelectronic Applications. *Chem. Mater.* **2023**, *35*, 2683–2712.
- (68) Kumar, D.; Verma, N. K.; Singh, C. B.; Singh, A. K.: Crystallite size strain analysis of nanocrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ perovskite by Williamson-Hall plot method. 2018.
- (69) Kumar, D.; Singh, C. B.; Verma, N. K.; Singh, A. K. Synthesis and structural investigations on multiferroic $\text{Ba}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskite manganites. *Ferroelectrics* **2017**, *518*, 191–195.
- (70) Sadabadi, H.; Allahkaram, S. R.; Kordijazi, A.; Akbarzadeh, O.; Rohatgi, P. K. Structural characterization of LaCoO_3 perovskite nanoparticles synthesized by sol–gel autocombustion method. *Eng. Rep.* **2021**, *3*, No. e12335.
- (71) Bokov, D.; Turki Jalil, A.; Chupradit, S.; Suksatan, W.; Javed Ansari, M.; Shewael, I. H.; Valiev, G. H.; Kianfar, E. Nanomaterial by Sol-Gel Method: Synthesis and Application. *Adv. Mater. Sci. Eng.* **2021**, *2021*, 5102014.
- (72) Navas, D.; Fuentes, S.; Castro-Alvarez, A.; Chavez-Angel, E. Review on Sol-Gel Synthesis of Perovskite and Oxide Nanomaterials. *Gels* **2021**, *7*, 275.
- (73) Kessler, V. G.: The Synthesis and Solution Stability of Alkoxide Precursors. In *Handbook of Sol-Gel Science and Technology: Processing, Characterization and Applications*; Klein, L., Aparicio, M., Jitianu, A., Eds.; Springer International Publishing: Cham, 2018; pp 31–80.
- (74) Andrade, V. M.; Vivas, R. J. C.; Pedro, S. S.; Tedesco, J. C. G.; Rossi, A. L.; Coelho, A. A.; Rocco, D. L.; Reis, M. S. Magnetic and magnetocaloric properties of $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ tunable by particle size and dimensionality. *Acta Mater.* **2016**, *102*, 49–55.
- (75) Wang, S.; Zhang, Y.; Zhu, J.; Tang, D.; Zhao, Z.; Yang, X. Sol-Gel Preparation of Perovskite Oxides Using Ethylene Glycol and Alcohol Mixture as Complexant and Its Catalytic Performances for CO Oxidation. *Chemistry select* **2018**, *3*, 12250–12257.
- (76) Haron, W.; Wisitsoraat, A.; Wongnawa, S. Nanostructured perovskite oxides – LaMO_3 (M = Al, Co, Fe) prepared by co-precipitation method and their ethanol-sensing characteristics. *Ceram. Int.* **2017**, *43*, 5032–5040.
- (77) Alkayal, N. S.; Hussein, M. A. Photocatalytic Degradation of Atrazine under Visible Light Using Novel $\text{Ag@Mg}_4\text{Ta}_2\text{O}_9$ Nanocomposites. *Sci. Rep.* **2019**, *9*, 7470.
- (78) Gaikwad, A. B.; Navale, S. C.; Samuel, V.; Murugan, A. V.; Ravi, V. A co-precipitation technique to prepare BiNbO_4 , MgTiO_3 and $\text{Mg}_4\text{Ta}_2\text{O}_9$ powders. *Mater. Res. Bull.* **2006**, *41*, 347–353.
- (79) Geetha, N.; Kumar, S.; Prakash, D. Synthesis and Characterization of $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ (X = 0, 0.1, 0.2) by Coprecipitation Route. *J. Phys. Chem. Biophys.* **2018**, *8*, 1–6.
- (80) Āšmontas, S.; Mujahid, M. Recent Progress in Perovskite Tandem Solar Cells. *Nanomater.* **2023**, *13*, 1886.
- (81) Yi, S.-S.; Jung, J.-Y. J. R. a. Barium molybdate white emitting phosphor synthesized at room temperature by co-precipitation. *RSC Adv.* **2022**, *12*, 21827–21835.
- (82) Grammatikopoulos, P.; Steinhauer, S.; Vernieres, J.; Singh, V.; Sowwan, M. Nanoparticle design by gas-phase synthesis. *Advances in Physics: X* **2016**, *1*, 81–100.
- (83) Kelesidis, G. A.; Pratsinis, S. E. A perspective on gas-phase synthesis of nanomaterials: Process design, impact and outlook. *Chemical Engineering Journal* **2021**, *421*, 129884.
- (84) Oke, J. A.; Jen, T.-C. Atomic layer deposition and other thin film deposition techniques: from principles to film properties. *Journal of Materials Research and Technology* **2022**, *21*, 2481–2514.
- (85) Liu, X.; Cao, L.; Guo, Z.; Li, Y.; Gao, W.; Zhou, L. A Review of Perovskite Photovoltaic Materials’ Synthesis and Applications via Chemical Vapor Deposition Method. *Materials* **2019**, *12*, 3304.
- (86) Xiu, Z. Preparation of tin-based perovskite solar cell thin films assisted by stannous fluoride. *Energy Reports* **2022**, *8*, 1079–1089.
- (87) Alami, A. H.; Alashkar, A.; Abdelkareem, M. A.; Rezk, H.; Masdar, M. S.; Olabi, A. G. Perovskite Membranes: Advancements and Challenges in Gas Separation, Production, and Capture. *Membranes* **2023**, *13*, 661.
- (88) Malik, S.; Muhammad, K.; Waheed, Y. Nanotechnology: A Revolution in Modern Industry. *Molecules* **2023**, *28*, 661.
- (89) Ludwig, T.; Bohr, C.; Queraltó, A.; Frohnhoven, R.; Fischer, T.; Mathur, S.: Inorganic nanofibers by electrospinning techniques and their application in energy conversion and storage systems. In *Semiconductors and Semimetals*; Elsevier: Amsterdam, 2018; Vol. 98; pp 1–70.
- (90) Cao, Y.; Lin, B.; Sun, Y.; Yang, H.; Zhang, X. Structure, morphology and electrochemical properties of $\text{La}_x\text{Sr}_{1-x}\text{CoO}_{3-\delta}$ perovskite nanofibers prepared by electrospinning method. *Journal of Alloys and compounds* **2015**, *624*, 31–39.
- (91) Zhen, D.; Zhao, B.; Shin, H. C.; Bu, Y.; Ding, Y.; He, G.; Liu, M. J. A. M. I. Electrospun porous perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ nanofibers for efficient oxygen evolution reaction. *Adv. Mater. Interfaces* **2017**, *4* (13), 1700146.
- (92) Wang, B.; Gu, S.; Ding, Y.; Chu, Y.; Zhang, Z.; Ba, X.; Zhang, Q.; Li, X. J. A. A novel route to prepare LaNiO_3 perovskite-type oxide nanofibers by electrospinning for glucose and hydrogen peroxide sensing. *Analyst* **2013**, *138*, 362–367.
- (93) Yuan, C.; Yang, Y.; Huang, L.; Xiao, Y. Integrating Low-Stack Photonic Crystals with the Honeycomb-like Structural Framework to Enhance the Photovoltaic Performance in Perovskite Solar Cells. *ACS Omega* **2024**, *9*, 9720.
- (94) Xu, H.; Ma, Y.; Chen, J.; Zhang, W.-x.; Yang, J. Electrocatalytic reduction of nitrate—a step towards a sustainable nitrogen cycle. *Chem. Soc. Rev.* **2022**, *51*, 2710–2758.
- (95) Wang, Y.; Wang, C.; Li, M.; Yu, Y.; Zhang, B. Nitrate electroreduction: mechanism insight, in situ characterization, performance evaluation, and challenges. *Chem. Soc. Rev.* **2021**, *50*, 6720–6733.
- (96) Garcia-Segura, S.; Lanzarini-Lopes, M.; Hristovski, K.; Westerhoff, P. Electrocatalytic reduction of nitrate: Fundamentals to full-scale water treatment applications. *Applied Catalysis B: Environmental* **2018**, *236*, 546–568.
- (97) Zhang, J.; Zhan, S.; Zhong, L.-B.; Wang, X.; Qiu, Z.; Zheng, Y.-M. Adsorption of typical natural organic matter on microplastics in aqueous solution: Kinetics, isotherm, influence factors and mechanism. *Journal of Hazardous Materials* **2023**, *443*, 130130.
- (98) Yao, D.; Gu, L.; Zuo, B.; Weng, S.; Deng, S.; Hao, W. A strategy for preparing high-efficiency and economical catalytic electrodes toward overall water splitting. *Nanoscale* **2021**, *13*, 10624–10648.
- (99) Hu, J.; Lim, F. Y.; Hu, J. Characteristics and behaviors of microplastics undergoing photoaging and Advanced Oxidation Processes (AOPs) initiated aging. *Water Res.* **2023**, *232*, 119628.
- (100) Gayen, P.; Spataro, J.; Avasarala, S.; Ali, A.-M.; Cerrato, J. M.; Chaplin, B. P. Electrocatalytic reduction of nitrate using magnéli phase TiO_2 reactive electrochemical membranes doped with Pd-based catalysts. *Environ. Sci. Technol.* **2018**, *52*, 9370–9379.
- (101) Shen, Z.; Liu, D.; Peng, G.; Ma, Y.; Li, J.; Shi, J.; Peng, J.; Ding, L. Electrocatalytic reduction of nitrate in water using Cu/Pd modified Ni foam cathode: High nitrate removal efficiency and N_2 -selectivity. *Sep. Purif. Technol.* **2020**, *241*, 116743.
- (102) Cerrón-Calle, G. A.; Fajardo, A. S.; Sánchez-Sánchez, C. M.; Garcia-Segura, S. Highly reactive Cu-Pt bimetallic 3D-electrocatalyst for selective nitrate reduction to ammonia. *Applied Catalysis B: Environmental* **2022**, *302*, 120844.

- (103) Liu, J.-X.; Richards, D.; Singh, N.; Goldsmith, B. R. Activity and selectivity trends in electrocatalytic nitrate reduction on transition metals. *ACS Catal.* **2019**, *9*, 7052–7064.
- (104) Wang, X.; Zhu, M.; Zeng, G.; Liu, X.; Fang, C.; Li, C. A three-dimensional Cu nanobelt cathode for highly efficient electrocatalytic nitrate reduction. *Nanoscale* **2020**, *12*, 9385–9391.
- (105) Wang, J.; Cai, C.; Wang, Y.; Yang, X.; Wu, D.; Zhu, Y.; Li, M.; Gu, M.; Shao, M. Electrocatalytic reduction of nitrate to ammonia on low-cost ultrathin CoO_x nanosheets. *ACS Catal.* **2021**, *11*, 15135–15140.
- (106) Gao, J.; Jiang, B.; Ni, C.; Qi, Y.; Zhang, Y.; Oturan, N.; Oturan, M. A. Non-precious Co₃O₄-TiO₂/Ti cathode based electrocatalytic nitrate reduction: Preparation, performance and mechanism. *Applied Catalysis B: Environmental* **2019**, *254*, 391–402.
- (107) Lan, Y.; Chen, J.; Zhang, H.; Zhang, W.-x.; Yang, J. Fe/Fe₃C nanoparticle-decorated N-doped carbon nanofibers for improving the nitrogen selectivity of electrocatalytic nitrate reduction. *Journal of Materials Chemistry A* **2020**, *8*, 15853–15863.
- (108) Zheng, W.; Zhu, L.; Yan, Z.; Lin, Z.; Lei, Z.; Zhang, Y.; Xu, H.; Dang, Z.; Wei, C.; Feng, C. Self-activated Ni cathode for electrocatalytic nitrate reduction to ammonia: from fundamentals to scale-up for treatment of industrial wastewater. *Environ. Sci. Technol.* **2021**, *55*, 13231–13243.
- (109) Song, Q.; Zhang, S.; Hou, X.; Li, J.; Yang, L.; Liu, X.; Li, M. Efficient electrocatalytic nitrate reduction via boosting oxygen vacancies of TiO₂ nanotube array by highly dispersed trace Cu doping. *Journal of Hazardous Materials* **2022**, *438*, 129455.
- (110) Liu, F.; Zhang, Z.; Shi, L.; Zhang, Y.; Qiu, X.; Dong, Y.; Jiang, H.; Zhu, Y.; Zhu, J. Promoting nitrate electroreduction to ammonia over A-site deficient cobalt-based perovskite oxides. *Journal of Materials Chemistry A* **2023**, *11*, 10596–10604.
- (111) Li, X.; Zhao, H.; Liang, J.; Luo, Y.; Chen, G.; Shi, X.; Lu, S.; Gao, S.; Hu, J.; Liu, Q.; Sun, X. A-site perovskite oxides: an emerging functional material for electrocatalysis and photocatalysis. *J. Mater. Chem. A* **2021**, *9*, 6650–6670.
- (112) Wang, J.; Wu, D.; Li, M.; Wei, X.; Yang, X.; Shao, M.; Gu, M. Bismuth ferrite as an electrocatalyst for the electrochemical nitrate reduction. *Nano Lett.* **2022**, *22*, 5600–5606.
- (113) Vijayaraghavan, K.; Balasubramanian, R. Application of pinewood waste-derived biochar for the removal of nitrate and phosphate from single and binary solutions. *Chemosphere* **2021**, *278*, 130361.
- (114) Liu, W.; Li, X.; Chu, X.; Zuo, S.; Gao, B.; Yao, C.; Li, Z.; Chen, Y. Boosting photocatalytic reduction of nitrate to ammonia enabled by perovskite/biochar nanocomposites with oxygen defects and O-containing functional groups. *Chemosphere* **2022**, *294*, 133763.
- (115) Karamad, M.; Goncalves, T. J.; Jimenez-Villegas, S.; Gates, I. D.; Siahrostami, S. Why copper catalyzes electrochemical reduction of nitrate to ammonia. *Faraday Discuss.* **2023**, *243*, 502.
- (116) Kang, X.; Zhu, Q.; Sun, X.; Hu, J.; Zhang, J.; Liu, Z.; Han, B. Highly efficient electrochemical reduction of CO₂ to CH₄ in an ionic liquid using a metal–organic framework cathode. *Chemical Science* **2016**, *7*, 266–273.
- (117) Qiu, W.; Liu, Y.; Xie, M.; Jin, Z.; Li, P.; Yu, G. Structural engineering of catalysts for ammonia electrosynthesis from nitrate: recent advances and challenges. *EES Catal.* **2024**, *2*, 202.
- (118) Wei, L.; Zhang, Y.; Zhang, C.; Yao, C.; Ni, C.; Li, X. In Situ Growth of Perovskite on 2D Hydrothermal Carbonation Carbon for Photocatalytic Reduction of Nitrate to Ammonia. *ACS Applied Nano Materials* **2023**, *6*, 13127–13136.
- (119) Penninger, M. W.; Kim, C. H.; Thompson, L. T.; Schneider, W. F. DFT analysis of NO oxidation intermediates on undoped and doped LaCoO₃ perovskite. *J. Phys. Chem. C* **2015**, *119*, 20488–20494.
- (120) Choi, S. O.; Penninger, M.; Kim, C. H.; Schneider, W. F.; Thompson, L. T. Experimental and computational investigation of effect of Sr on NO oxidation and oxygen exchange for La_{1-x}Sr_xCoO₃ perovskite catalysts. *ACS Catal.* **2013**, *3*, 2719–2728.
- (121) Zhou, C.; Liu, X.; Wu, C.; Wen, Y.; Xue, Y.; Chen, R.; Zhang, Z.; Shan, B.; Yin, H.; Wang, W. G. NO oxidation catalysis on copper doped hexagonal phase LaCoO₃: a combined experimental and theoretical study. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5106–5112.
- (122) Zhang, W.; Li, F.; Zhang, W.; Wang, Y.; Liu, S.; Mo, X.; Li, K. B-site cation synergy in Mn doped LaCoO₃ for enhanced electrocatalysts for electrochemical reduction of nitrate. *Sep. Purif. Technol.* **2023**, *317*, 123775.
- (123) Guan, D.; Zhou, J.; Huang, Y.-C.; Dong, C.-L.; Wang, J.-Q.; Zhou, W.; Shao, Z. Screening highly active perovskites for hydrogen-evolving reaction via unifying ionic electronegativity descriptor. *Nat. Commun.* **2019**, *10*, 3755.
- (124) Zhang, H.; Xu, Y.; Lu, M.; Xie, X.; Huang, L. Perovskite Oxides for Cathodic Electrocatalysis of Energy-Related Gases: From O₂ to CO₂ and N₂. *Adv. Funct. Mater.* **2021**, *31*, 2101872.
- (125) Hwang, J.; Rao, R. R.; Giordano, L.; Katayama, Y.; Yu, Y.; Shao-Horn, Y. Perovskites in catalysis and electrocatalysis. *Science* **2017**, *358*, 751–756.
- (126) Chu, K.; Zong, W.; Xue, G.; Guo, H.; Qin, J.; Zhu, H.; Zhang, N.; Tian, Z.; Dong, H.; Miao, Y.-E.; Roeyffers, M. B. J.; Hofkens, J.; Lai, F.; Liu, T. Cation Substitution Strategy for Developing Perovskite Oxide with Rich Oxygen Vacancy-Mediated Charge Redistribution Enables Highly Efficient Nitrate Electroreduction to Ammonia. *J. Am. Chem. Soc.* **2023**, *145*, 21387–21396.
- (127) Geng, J.; Ji, S.; Xu, H.; Zhao, C.; Zhang, S.; Zhang, H. Electrochemical reduction of nitrate to ammonia in a fluidized electrocatalysis system with oxygen vacancy-rich CuO_x nanoparticles. *Inorganic Chemistry Frontiers* **2021**, *8*, 5209–5213.
- (128) Liu, Y.; Deng, P.; Wu, R.; Zhang, X.; Sun, C.; Li, H. Oxygen vacancies for promoting the electrochemical nitrogen reduction reaction. *Journal of Materials Chemistry A* **2021**, *9*, 6694–6709.
- (129) Zhu, H.; Wang, C.; He, Y.; Pu, Y.; Li, P.; He, L.; Huang, X.; Tang, W.; Tang, H. Oxygen vacancies engineering in electrocatalysts nitrogen reduction reaction. *Front. Chem.* **2022**, *10*, 1039738.
- (130) Yang, L.-H.; Lin, Z.-Q.; Liao, M.-T.; Yang, W.-J.; Pan, J.-X.; Li, W.; Yang, C.; Wu, Y.-J.; Wang, G.-Z.; Lv, S.-H. Engineering oxygen vacancies in perovskite oxides by in-situ electrochemical activation for highly efficient nitrate reduction. *Appl. Surf. Sci.* **2023**, *639*, 158208.
- (131) Chu, K.; Qin, J.; Zhu, H.; De Ras, M.; Wang, C.; Xiong, L.; Zhang, L.; Zhang, N.; Martens, J. A.; Hofkens, J.; Lai, F.; Liu, T. High-entropy perovskite oxides: A versatile class of materials for nitrogen reduction reactions. *Sci. China Mater.* **2022**, *65*, 2711–2720.
- (132) Wang, T.; Fan, J.; Do-Thanh, C. L.; Suo, X.; Yang, Z.; Chen, H.; Yuan, Y.; Lyu, H.; Yang, S.; Dai, S. Perovskite oxide–halide solid solutions: A platform for electrocatalysts. *Angew. Chem.* **2021**, *133*, 10041–10046.
- (133) Fan, X.; Zhao, D.; Deng, Z.; Zhang, L.; Li, J.; Li, Z.; Sun, S.; Luo, Y.; Zheng, D.; Wang, Y.; Ying, B.; Zhang, J.; Alshehri, A. A.; Lin, Y.; Tang, C.; Sun, X.; Zheng, Y. Constructing Co@TiO₂ nanoarray heterostructure with schottky contact for selective electrocatalytic nitrate reduction to ammonia. *Small* **2023**, *19*, 2208036.
- (134) Wu, Q.; Zhu, W.; Ma, D.; Liang, C.; Wang, Z.; Liang, H. Screening of transition metal oxides for electrocatalytic nitrate reduction to ammonia at large currents. *Nano Res.* **2024**, *17*, 3902.
- (135) Li, K.; Zhang, S.; Li, Y.; Fan, J.; Lv, K. MXenes as noble-metal-alternative co-catalysts in photocatalysis. *Chinese Journal of Catalysis* **2021**, *42*, 3–14.
- (136) Zhang, F.; Zhu, Y.; Lin, Q.; Zhang, L.; Zhang, X.; Wang, H. Noble-metal single-atoms in thermocatalysis, electrocatalysis, and photocatalysis. *Energy Environ. Sci.* **2021**, *14*, 2954–3009.
- (137) Martín, A. J.; Mitchell, S.; Mondelli, C.; Jaydev, S.; Pérez-Ramírez, J. Unifying views on catalyst deactivation. *Nature Catalysis* **2022**, *5*, 854–866.
- (138) Liotta, L. F. Catalytic oxidation of volatile organic compounds on supported noble metals. *Applied Catalysis B: Environmental* **2010**, *100*, 403–412.
- (139) Hu, C.; Paul, R.; Dai, Q.; Dai, L. Carbon-based metal-free electrocatalysts: from oxygen reduction to multifunctional electrocatalysis. *Chem. Soc. Rev.* **2021**, *50*, 11785–11843.

- (140) Jia, Y.; Yao, X. Defects in carbon-based materials for electrocatalysis: synthesis, recognition, and advances. *Acc. Chem. Res.* **2023**, *56*, 948–958.
- (141) Feng, W.; Pang, W.; Xu, Y.; Guo, A.; Gao, X.; Qiu, X.; Chen, W. Transition metal selenides for electrocatalytic hydrogen evolution reaction. *ChemElectroChem.* **2020**, *7*, 31–54.
- (142) Zhang, Y.; Zhou, Q.; Zhu, J.; Yan, Q.; Dou, S. X.; Sun, W. Nanostructured metal chalcogenides for energy storage and electrocatalysis. *Adv. Funct. Mater.* **2017**, *27*, 1702317.
- (143) Wang, T.; Legut, D.; Fan, Y.; Qin, J.; Li, X.; Zhang, Q. Building fast diffusion channel by constructing metal sulfide/metal selenide heterostructures for high-performance sodium ion batteries anode. *Nano Lett.* **2020**, *20*, 6199–6205.
- (144) Li, S.; Wang, S.; Wang, J. Optimal surface/diffusion-controlled kinetics of bimetallic selenide nanotubes for hybrid supercapacitors. *J. Colloid Interface Sci.* **2022**, *617*, 304–314.
- (145) Li, Y.; Hou, P.; Xi, Z.; Xu, Y.; Liu, Y.; Tian, H.; Li, J.; Yang, Y.; Deng, Y.; Wu, D. Charge transfer driving interfacial reconstructions in perovskite oxide heterostructures. *Communications Physics* **2023**, *6*, 70.
- (146) Hong, W. T.; Stoerzinger, K. A.; Lee, Y.-L.; Giordano, L.; Grimaud, A.; Johnson, A. M.; Hwang, J.; Crumlin, E. J.; Yang, W.; Shao-Horn, Y. Charge-transfer-energy-dependent oxygen evolution reaction mechanisms for perovskite oxides. *Energy Environ. Sci.* **2017**, *10*, 2190–2200.
- (147) Sun, X.; Li, M.; Qiu, Q.; Song, J.; Zhu, L.; Qiang, Y. Charge transfer enhancement of TiO₂/perovskite interface in perovskite solar cells. *Journal of Materials Science: Materials in Electronics* **2021**, *32*, 22936–22943.