

# Recent Advances on the Gas-Sensing Properties and Mechanism of Perovskite Oxide Materials - A Review

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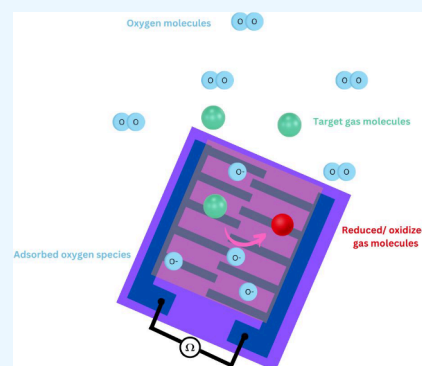
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**ABSTRACT:** Perovskite oxide-based materials ( $\text{ABO}_3$ ) have gained much attention as promising candidates for advanced gas-sensing applications due to their versatile structures, tunable properties, and excellent stability. This review discusses recent developments in the synthesis, structural optimization, and functionalization of perovskites to enhance their gas-sensing performance. Strategies such as doping, creating oxygen vacancies, tuning morphology, and forming heterojunctions have significantly improved their sensitivity, selectivity, response, and recovery times. Specific advances include the incorporation of nanostructures, porous morphologies, and catalytic elements, which have optimized the adsorption and desorption processes for various target gases, including volatile organic compounds,  $\text{NO}_2$ , and  $\text{CO}_2$ . Mechanistic insights into the role of oxygen vacancies, surface defects, and charge carrier dynamics are also addressed. These developments position perovskite materials as important components in next-generation gas sensors for environmental monitoring and industrial applications.



## 1. INTRODUCTION

In recent decades, rapid urban and industrial expansion has led to severe air pollution. Poor air quality poses considerable dangers to human health, especially from the leakage of flammable and toxic gases. As a result, gas sensing technologies have become crucial for monitoring air quality, detecting hazardous gases, and identifying volatile organic compounds (VOCs), as well as in medical diagnostics. Recently, numerous gas sensors have been developed and categorized based on their sensing mechanisms, including thermal conductivity, semiconductor metal oxides (SMOs), infrared absorption, catalytic combustion, electrochemical, and solid electrolyte sensors. Among these, SMO-based gas sensors have emerged as highly promising candidates due to their cost-effectiveness, high sensitivity, ease of use, miniaturization, and flexible fabrication processes.<sup>1,2</sup> Various SMO nanocomposites, such as tin oxide ( $\text{SnO}_2$ ),<sup>3</sup> zinc oxide ( $\text{ZnO}$ ),<sup>4</sup> and ferric oxide ( $\text{Fe}_2\text{O}_3$ ),<sup>5</sup> have been explored for detecting different gases across various applications. Despite this progress, still some challenges exist in developing gas sensors that offer excellent selectivity, high sensitivity, fast response and recovery times, low detection limits, reliable repeatability, long-term stability, and strong resistance to humidity.<sup>6</sup>

In recent years, research has increasingly focused on the development of innovative low-dimensional nanomaterials to boost the gas sensors' performance. Materials such as graphene,<sup>7</sup> carbon nanotubes,<sup>8</sup> metal oxides,<sup>3</sup> and perovskites<sup>9</sup> have

emerged as promising candidates due to their excellent electrical properties, mechanical strength, and high surface-to-volume ratios. These materials have demonstrated high sensitivity to gases like  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$ , and  $\text{CO}_2$ , making them valuable for advanced sensing applications.<sup>10</sup>

The perovskite structure was first discovered by Gustav Rose in 1839 in Russia, within the naturally occurring mineral  $\text{CaTiO}_3$ . Since then, other minerals and synthetic compounds with the general formula  $\text{ABX}_3$  have been found to share a structure similar to that of  $\text{CaTiO}_3$ , and these are broadly referred to as perovskites. In this structure, the "A" site typically consists of an alkali metal ( $\text{A}^+$ ), an alkaline earth metal ( $\text{A}^{2+}$ ), or a transition-metal cation ( $\text{A}^{3+}$ ) with 12-fold coordination. The "B" site is occupied by transition-metal cations ( $\text{B}^{3+}$ ,  $\text{B}^{4+}$ , or  $\text{B}^{5+}$ ) with a 6-fold coordination, while "X" represents anions such as oxygen, carbon, nitrogen, or halogens.<sup>11</sup> This kind of material shows good thermal stability and band gap of 3–4 eV and was utilized in several gas sensing studies.<sup>12</sup> Partially or fully replacing A or B cations in the perovskite structure with lower valence cations, reducing their total charge to less than 6+,

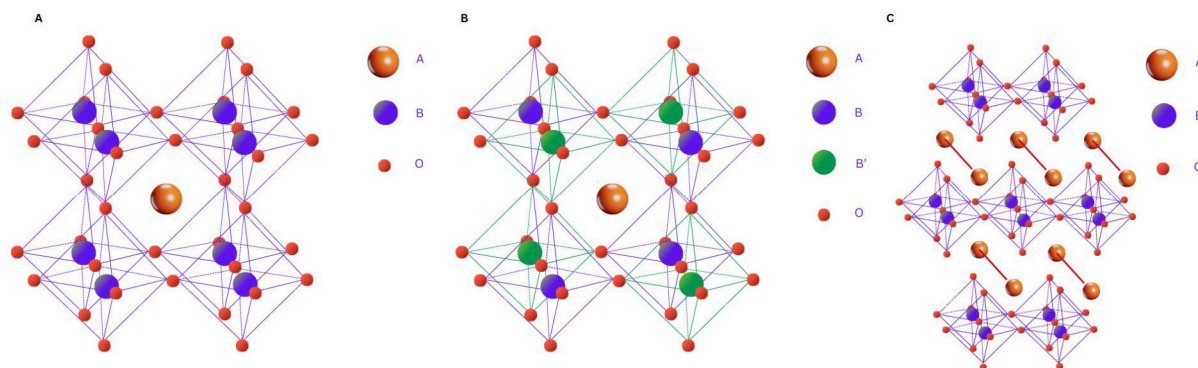
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**Figure 1.** Schematic illustration of the A) simple perovskite structure, B) double perovskite, and C) layered perovskite.

creates vacancies in the oxygen lattice. This modification enables mixed ionic and electronic conductivities, where the transition-metal cations contribute to electronic conductivity. Nanomaterial-based perovskite materials have shown excellent sensing ability toward different gases such as HCHO,<sup>9</sup> CO,<sup>13</sup> CO,<sup>14</sup> CH<sub>3</sub>OH,<sup>15</sup> H<sub>2</sub>,<sup>16</sup> etc.

ABO<sub>3</sub> perovskites are promising candidates for resistive-type gas sensors due to several key factors: (1) the structural stability provided by the abundance of metallic elements in the perovskite composition,<sup>17</sup> (2) the ability to modify the structure and chemical composition through partial substitution of A and/or B cations with aliovalent elements of different sizes and valences,<sup>18,19</sup> (3) the preservation of structural integrity despite deviations from stoichiometry,<sup>20</sup> and (4) their distinctive electronic structure and high electron mobility.<sup>21</sup> In perovskites, oxygen-deficient vacancies are more common than cationic vacancies, likely because anionic vacancies require less energy to form.<sup>22</sup> The presence of both cationic and oxygen vacancies enhances their electrical and redox properties, as well as their catalytic behavior, which significantly impacts gas-sensing capabilities. Their mechanical and thermal stability also makes them suitable for sensing applications over a wide temperature range.

The performance of chemiresistive gas sensors is influenced by environmental factors, such as humidity, operating temperature, and gas concentration. Key parameters include the limit of detection, response/recovery times, sensitivity, selectivity, drift, and reversibility. An ideal sensor exhibits fast response/recovery, high sensitivity and selectivity, and full recovery without drift.<sup>23</sup> Using perovskite oxides for chemiresistive sensors presents challenges due to the high-temperature heat treatment required to achieve a well-defined crystalline phase. However, this process can paradoxically lead to significant grain growth in perovskite oxide nanostructures, reducing the active surface area available for gas interactions and ultimately impairing sensing performance.<sup>24</sup> Additionally, the inherently low surface activity of perovskite oxides has limited their application in chemiresistive sensors. This limitation is largely due to their p-type semiconducting behavior, which is dominated by positive charge carriers. As noted by Hübner et al., p-type oxide sensors typically exhibit a response proportional to the square root of the gas concentration under identical morphological configurations.<sup>25</sup> Despite these challenges, ongoing research efforts aim to overcome these limitations and improve the sensing performance of p-type perovskite oxide-based sensors.

Understanding the fundamental sensing mechanisms and influential factors on sensing performance provides comprehensive knowledge to overcome perovskite oxide gas sensor

limitations. In recent years, numerous review articles have explored perovskite oxide-based gas sensors,<sup>26–28</sup> often focusing on specific aspects such as synthesis methods, structural properties, or applications for detection of specific gases. Singh et al.<sup>27</sup> reviewed recent advances in perovskite-based sensors for VOC detection, emphasizing their role in early disease diagnosis. They compared metal halide and metal oxide perovskites, analyzing their sensing mechanisms, structural differences, and synthesis methods. Key factors affecting performance are also discussed. Souri et al.<sup>28</sup> reviewed recent progress in room-temperature perovskite gas sensors, highlighting their high sensitivity, selectivity, and stability. They discussed key factors affecting performance including dopants, oxygen vacancies, and surface morphology. The study emphasizes the importance of understanding sensing mechanisms to advance perovskite-based gas sensors for practical applications.

This review provides a distinct contribution by integrating insights into fundamental sensing mechanisms with advanced material design strategies. This paper emphasizes the role of oxygen vacancies, surface defects, and heterojunctions in enhancing charge carrier dynamics and gas adsorption. Furthermore, we present a comprehensive overview of cutting-edge synthesis techniques, including the use of metal–organic frameworks (MOFs) and other innovative methods, while linking these advancements to their impact on sensor performance. Additionally, this review expands the scope to include a broad range of target gases, such as VOCs, NO<sub>2</sub>, and CO<sub>2</sub>, and highlights the interplay between morphology, composition, and functionality. These aspects position this article as a valuable resource for advancing perovskite-based gas sensor research, addressing key gaps in understanding and practical application. It also summarizes current performance metrics and discusses the challenges that need to be addressed while suggesting new directions for future applications.

## 2. CLASSIFICATION OF THE PEROVSKITE OXIDE MATERIALS

Perovskite oxides can be broadly classified into three main categories: simple, double, and layered perovskites. Approximately 90% of metallic elements are known to crystallize in the perovskite structure, as oxides and halides can form various morphologies, including isotropic, anisotropic, and amorphous forms. 1- Simple Perovskites (ABO<sub>3</sub>): In these structures, the A-site cation is typically a larger alkali, alkaline earth, or rare earth metal coordinating with 12 oxygen atoms. The B-site is a smaller transition metal cation, forming BO<sub>6</sub> octahedra that share

corners (Figure 1). This coordination remains stable when the ionic radii of A ( $r_A$ ), B ( $r_B$ ), and O ( $r_O$ ) ions fall within the constraints defined by Goldschmidt tolerance factor,  $t$ :<sup>29</sup>

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

A tolerance factor between 0.9–1 is favorable for formation of the stable perovskite structure.<sup>30</sup> The ideal perovskite structure with a cubic system has tolerance factor of 1.<sup>31</sup> 2- Double Perovskite Oxides ( $AA'BB'O_6$ ): These structures feature corner-sharing  $BO_6$  and  $B'O_6$  octahedra, with A and A' positions occupied by alkali, alkaline earth, or rare earth metal cations. The difference in the sizes of the B and B' cations influences the degree of ordering within the structure. Ordering of cations on the A and B sites can significantly alter the physical properties of double perovskites.<sup>32</sup> 3- Layered Perovskite Oxides: These structures are derived from simple perovskites ( $ABO_3$ ) by cutting along the (001) direction and adding extra oxygen layers. They are further categorized into Aurivillius, Ruddlesden–Popper, and Dion–Jacobson oxides depending on the interlayer cations present. The structural diversity and symmetry of perovskite oxides give them unique physicochemical properties, influencing their functionality as gas sensors, which will be discussed in subsequent sections.

### 3. RECENT ADVANCES IN SYNTHESIS AND FABRICATION TECHNIQUES

Perovskite oxide ceramics are synthesized by using various physical and chemical properties inherent to the materials. The conventional ceramic method, which involves solid-state reactions at high temperatures, is commonly employed for producing these materials.<sup>33</sup> However, the traditional ceramic synthesis using solid-state reactions presents some limitations, such as the need for repeated grinding and heating of metal oxides or their salts before calcination.<sup>34</sup> These drawbacks include product inhomogeneity, the presence of defects that can affect luminescence, contamination from grinding and heating, and coarse particles that cannot be used for coatings.<sup>35</sup>

Future research should focus on refining the preparation process to enhance the charge transfer and storage capacity by adjusting the morphology or integrating other materials. Therefore, various preparation methods are detailed to aid in choosing the most suitable approach for different substances. Effective synthesis of perovskite materials with customizable morphologies is crucial for in-depth analysis of their microstructure and electrochemical properties. Different preparation techniques significantly influence the material's size, structural morphology, and electrochemical performance. To address these issues and obtain purer materials, several alternative synthesis techniques have been developed, including coprecipitation,<sup>36</sup> hydrothermal synthesis,<sup>37</sup> solid-state reactions,<sup>38</sup> the Pechini method,<sup>39</sup> sol–gel,<sup>40</sup> microwave synthesis,<sup>14</sup> physical vapor deposition (PVD) methods like laser ablation,<sup>41</sup> wet chemical techniques, and some other methods<sup>42</sup> (Figure 2).

**3.1. Coprecipitation Method.** This technique is commonly used for synthesizing simple oxides like  $ZnO$ .<sup>43</sup> It involves precipitation of metal salts by adding a reagent that lowers solubility. Coprecipitation occurs by the simultaneous precipitation of different cations. For uniform product formation, it is essential to control temperature, concentration, pH, and solution homogeneity. Common reagents for precipitation include ammonia, urea, ammonium oxalate, and

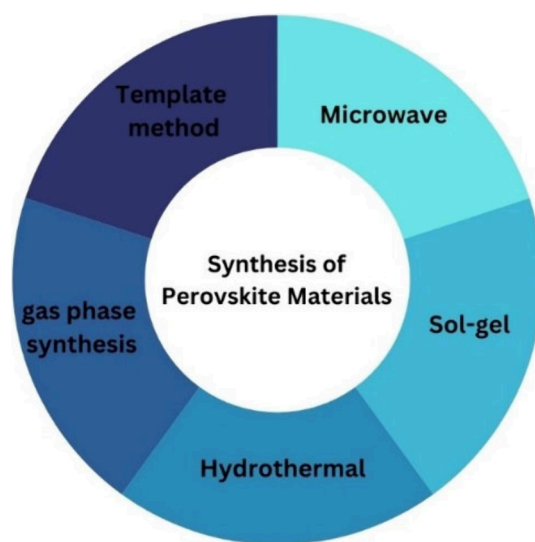


Figure 2. Perovskite materials synthesis methods.

ammonium carbonate. The resulting oxide compounds, which are insoluble, form through the thermal decomposition of hydroxides or organic/carbonate salts.<sup>44</sup> Coprecipitation due to simplicity, ease of control, cost-effective, and broad variation can be a promising method for synthesis of gas-sensing nanomaterials.<sup>45</sup> Recently, a coprecipitation method was applied for synthesis of Zn-doped  $In_2O_3$  with starfish-like dendritic structures and used for triethylamine (TEA) sensing at ppb-level selectively.<sup>46</sup>

**3.2. Solid-State Reactions.** In these reactions, both the starting materials and the final products are solids. Reagents like carbonates, nitrates, or oxides are mixed in stoichiometric ratios<sup>47</sup> and generally without addition of solvents, perovskite materials with large particle size and limited specific surface area provides.<sup>48</sup> For perovskite synthesis, oxides or carbonates of A- and B-site metal ions are combined according to the formula  $ABO_3$ . This process requires temperatures above two-thirds of the melting point and may last up to 10 h to achieve the desired composition. The materials are ball-milled in isopropanol or acetone, dried at 100 °C, then calcined for 4–8 h at 600 °C with controlled temperature cycles (2 °C/min). Further grinding, sieving, and recalcination at 1300–1600 °C for 5–15 h ensure a single-phase perovskite formation.<sup>49</sup>

**3.3. Hydrothermal Synthesis.** This method involves carrying out reactions in an aqueous solution or suspending the precursors at elevated temperatures and pressure. It is a simple and cost-effective method which allows to produce crystalline powders without calcination<sup>50</sup> with increased chemical reactivity.<sup>51</sup> This method enables control over particle size and shape through temperature, pH, time, and reactant concentration.<sup>52</sup> Recent advancements include synthesizing  $NiTiO_3$  perovskite nanoparticles (NPs) at various reaction times, and it was reported that band gap decreases by increasing the reaction time and maximum response to  $CO_2$  gas at room temperature (RT) obtained after 24 h reaction time.<sup>53</sup>

**3.4. Gas-Phase Preparations.** This approach is used to deposit perovskite films with specific structures and thicknesses.<sup>54</sup> Techniques vary based on temperature: direct deposition at crystallization temperature, intermediate deposition followed by postannealing (873–1073 K), or deposition at a low substrate temperature followed by high-temperature annealing.<sup>49</sup>



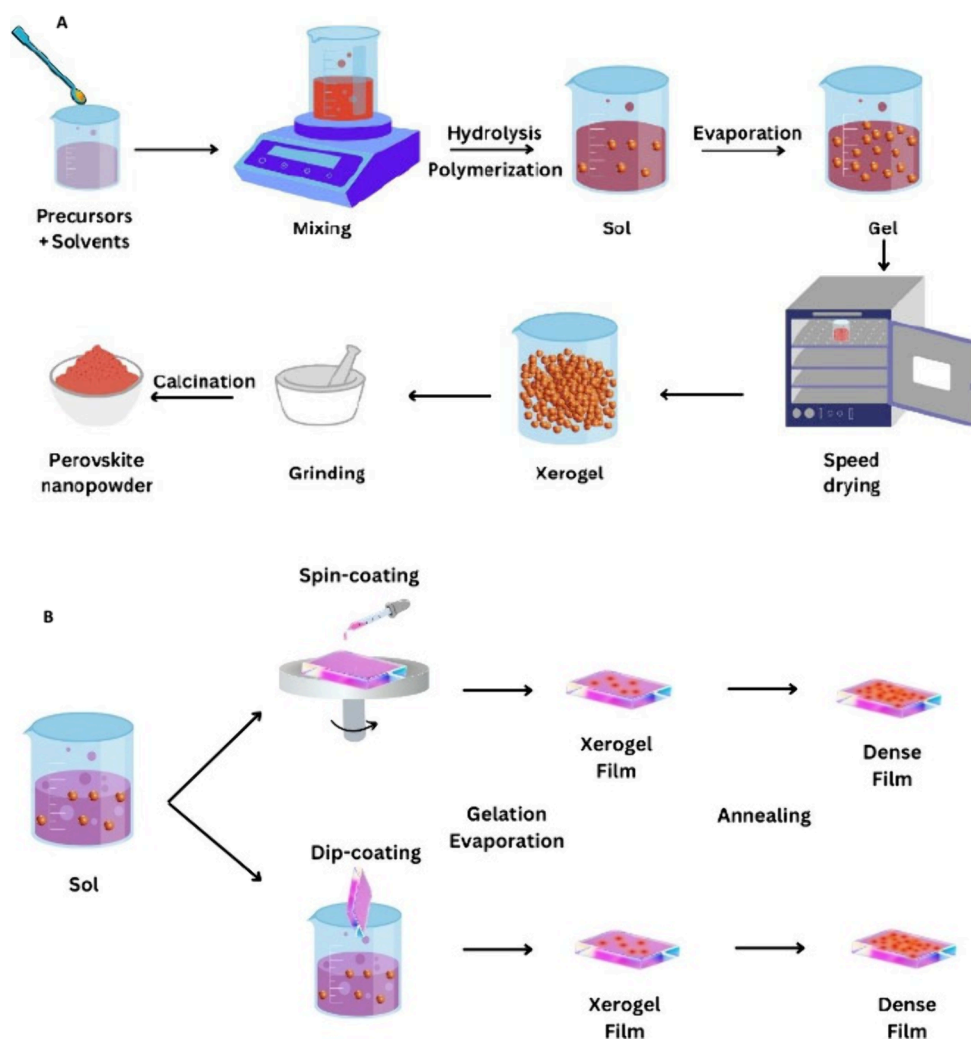


Figure 3. A) Schematic illustration of the sol-gel synthesis process and B) thin film processing.

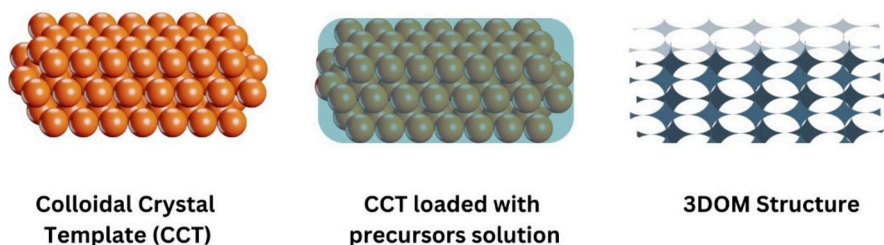


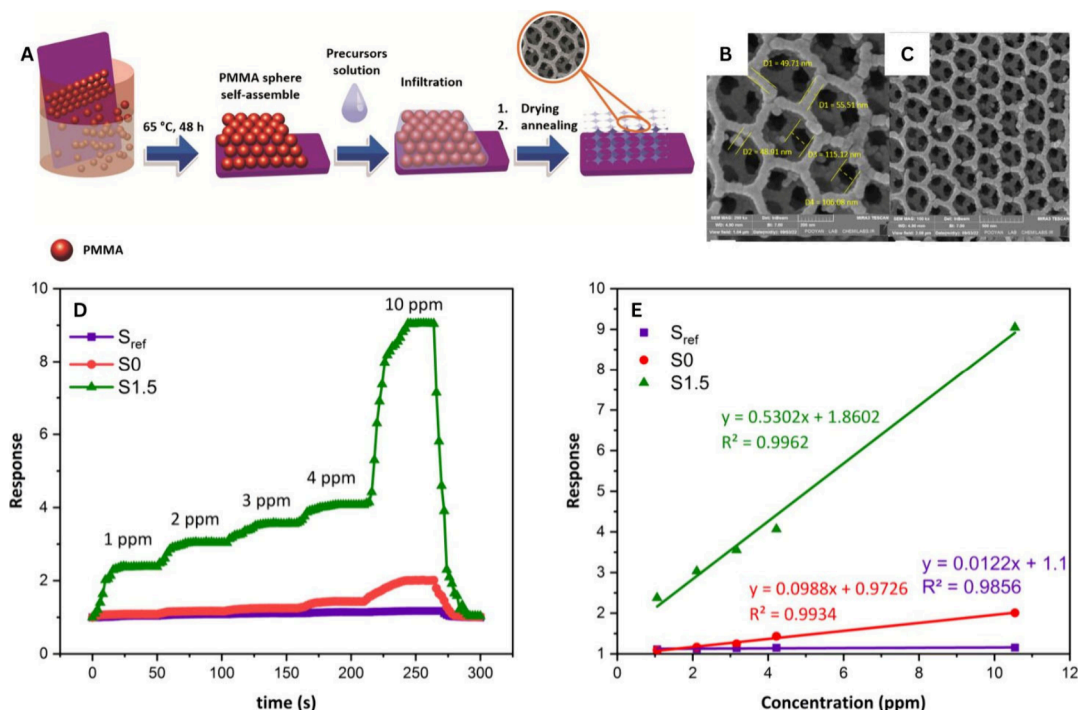
Figure 4. Schematic illustration of the colloidal-crystal-template (CCT) synthesis method.

**3.5. Sol-Gel Method.** This technique involves the hydrolysis and poly condensation of metallic alkoxides, which are commercially available for various metals.<sup>55</sup> The sol-gel method used for preparing nanosized materials and thin films allows control of the particle size of the composites, and very pure homogeneous materials and uniform nanomaterials at low temperatures can be obtained.<sup>56</sup> A schematic illustration of the sol-gel synthesis process is represented in Figure 3-A. However, its application is limited by precursor stability and challenges in controlling the composition of complex oxides, also by the requirement of different complexing agents, long reaction times, and special conditions (pH, temperature, etc.).<sup>57,58</sup> Aqueous sol-gel processes often use inorganic salts and carboxylic acids or polyols as chelating agents.<sup>59</sup> A schematic view of the sol-gel

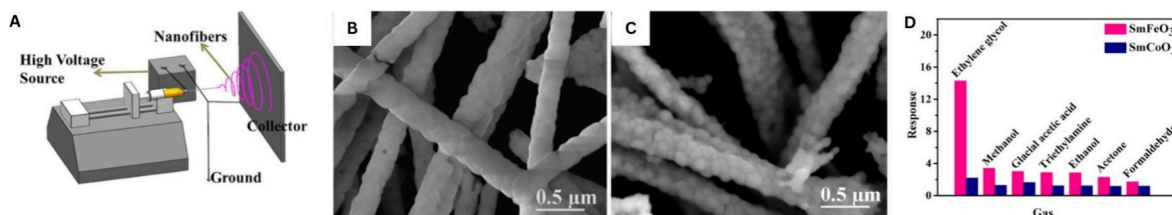
process for the development of thin films is shown in Figure 3-B. A sol-gel synthesis of modified  $\text{LaCrO}_3$  thin film prepared by spin coating represented rapid response and recovery time for CO,  $\text{CO}_2$ , and LPG.<sup>60</sup> Recently sol-gel synthesized CNT-doped  $\text{LaFeO}_3$  showed superior sensing ability toward LPG gas due to its porous structure and higher surface activity.<sup>61</sup>

**3.6. Microwave Synthesis.** Microwave irradiation offers a time- and energy-efficient alternative for synthesizing perovskite oxides.<sup>62</sup> It can be combined with other techniques such as sol-gel or hydrothermal synthesis to enhance control over stoichiometry and phase formation.<sup>63</sup> Microwave synthesis is particularly effective for synthesizing Pb-containing perovskites due to minimized lead loss.<sup>62</sup> Recently, Gildo-Ortiz et al. employed a simple and economical microwave-assisted solution





**Figure 5.** A) Schematic illustration of a synthetic process for 3DOM In-doped  $\text{SmFeO}_3$ , B, C) SEM images, and D, E) dynamic response transition of 3DOM In-doped  $\text{SmFeO}_3$  toward different concentrations of formaldehyde gas. Reproduced with permission from.<sup>9</sup>



**Figure 6.** A) Schematic illustrations of the electrospinning setup, SEM images of B)  $\text{SmFeO}_3$  and C)  $\text{SmCoO}_3$ , and D) selectivity of the samples toward different gases. Reproduced with permission from.<sup>69</sup>

method to produce  $\text{LaFeO}_3$  nanocrystalline perovskites. As a result, nanomaterials with high sensitivity to CO were obtained at lower temperature in comparison to those from a solid-state synthesis method.<sup>14</sup>

**3.7. Other Synthesis Methods.** The colloidal-crystal-template (CCT) method is another synthesis procedure to prepare nanoporous and three-dimensionally ordered macropore (3DOM) perovskite materials. In this method organic polymer spheres are used as a template to produce pores with different sizes in inorganic materials (Figure 4).<sup>64</sup> Recently, Soury et al. has used poly(methyl methacrylate) (PMMA) for the synthesis of highly sensitive In-doped  $\text{SmFeO}_3$  for the detection of the formaldehyde gas (Figure 5).<sup>9</sup>

The Pechini Method, also known as the polymeric precursor or mixed liquid method, enables precise control over reaction stoichiometry and provides high reproducibility and homogeneity.<sup>50</sup> This method offers fabrication of uniform, highly pure perovskite materials at low temperature.<sup>65</sup> It involves forming a chelate through the reaction of metal cations with a carboxylic acid, followed by heating a mixture of metal salts, citric acid, and ethylene glycol (80–100 °C) to form a clear solution. Further heating (150–250 °C) induces condensation reactions that lead to a polyester "resin" in which metal cations are uniformly distributed.<sup>66</sup> Derakhshi et al. employed Pechini sol–gel

method for the synthesis of  $\text{LaFe}_{0.4}\text{Cu}_{0.6}\text{O}_3$  perovskites, which results in 6.5 times higher response to 300 ppm ethanol at 300 °C compared to  $\text{LaFeO}_3$ .<sup>67</sup>

Electrospinning is a method used to produce nanofibers with diameters below 100 nm and lengths extending up to several kilometers. This technique employs an electrostatically driven jet of a polymer fluid stream under a high-voltage electric field. Electrospinning has attracted significant interest across numerous fields, such as sensor technology, due to its capability to create continuous fibers with diameters as small as a few nanometers and its adaptability to different compositions, including polymers, polymer blends, polymers embedded with nanoparticles, and metal oxides.<sup>68</sup> Han et al. have studied the gas sensing properties of  $\text{SmFeO}_3$  and  $\text{SmCoO}_3$  gas sensors prepared by electrospinning methods toward ethylene glycol at the optimal working temperature of 200 °C.<sup>69</sup> Results have indicated that the  $\text{SmFeO}_3$  nanofiber showed 6.5 times higher response than  $\text{SmCoO}_3$  toward 100 ppm ethylene glycol (Figure 6).

Various synthetic methods for perovskite materials, such as hydrothermal, sol–gel, solid-state reaction, microwave-assisted, and combustion techniques, typically require high calcination temperatures (above 800 °C) for several hours to achieve good crystallinity, resulting in larger particle sizes. The summary of

each synthesis method is given in Table 1. Electrodeposition, however, is a simple, safe, controllable, and environmentally

**Table 1. Summary of the pros and cons of different synthesis methods of perovskite materials**

Synthesis Method	Advantages	Disadvantages
Solid-State Reaction	<ul style="list-style-type: none"> <li>- Simple and cost-effective</li> <li>- Suitable for large-scale production</li> <li>- Produces stable crystalline structures</li> </ul>	<ul style="list-style-type: none"> <li>- High temperature required (<math>\sim 1000</math>–<math>1500</math> °C)</li> <li>- Long processing time</li> <li>- Poor control over particle size and morphology</li> </ul>
Sol–Gel Method	<ul style="list-style-type: none"> <li>- Low-temperature synthesis</li> <li>- Good chemical homogeneity</li> <li>- Precise control over composition and morphology</li> </ul>	<ul style="list-style-type: none"> <li>- Time-consuming</li> <li>- Requires organic solvents</li> <li>- Risk of impurity incorporation</li> </ul>
Hydrothermal Synthesis	<ul style="list-style-type: none"> <li>- Low-temperature process</li> <li>- Produces high-purity and crystalline materials</li> <li>- Enables controlled morphology (nanorods, nanospheres)</li> </ul>	<ul style="list-style-type: none"> <li>- Requires high-pressure conditions</li> <li>- Limited scalability for industrial applications</li> <li>- Long reaction times</li> </ul>
Coprecipitation	<ul style="list-style-type: none"> <li>- Simple and cost-effective</li> <li>- Produces homogeneous materials</li> <li>- Scalable for large-scale production</li> </ul>	<ul style="list-style-type: none"> <li>- Requires careful pH control</li> <li>- Post-treatment needed to enhance crystallinity</li> <li>- Risk of agglomeration</li> </ul>
Pechini Method	<ul style="list-style-type: none"> <li>- Produces fine, uniform powders</li> <li>- Good compositional control</li> <li>- Lower calcination temperature compared to solid-state synthesis</li> </ul>	<ul style="list-style-type: none"> <li>- Involves complex organic chemistry</li> <li>- Requires long processing steps</li> <li>- Expensive reagents needed</li> </ul>
Microwave-Assisted Synthesis	<ul style="list-style-type: none"> <li>- Rapid heating and reaction</li> <li>- Energy-efficient</li> <li>- Produces small and uniform particles</li> </ul>	<ul style="list-style-type: none"> <li>- Limited scalability</li> <li>- Requires special equipment</li> <li>- Not suitable for all perovskite compositions</li> </ul>
Electrochemical Deposition	<ul style="list-style-type: none"> <li>- Precise thickness and composition control</li> <li>- Low temperature</li> <li>- Environmentally friendly</li> </ul>	<ul style="list-style-type: none"> <li>- Limited to thin films</li> <li>- Requires conductive substrates</li> <li>- Slow deposition rate</li> </ul>

friendly method that has been widely employed to prepare perovskite materials under milder conditions.<sup>70,71</sup>

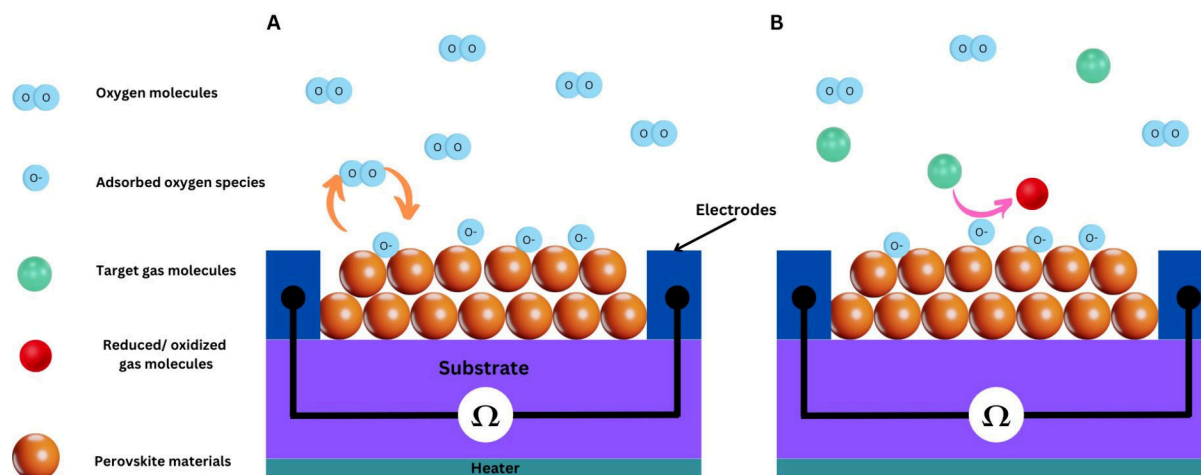
Electrochemical methods, such as anodic oxidation, cathodic reduction, and alternating current synthesis, are used to fabricate perovskite oxide thin films. These methods offer advantages like precise control over composition, lower synthesis temperatures compared to traditional solid-state reactions, and cost-effectiveness.<sup>72</sup> For example, researchers have successfully synthesized  $\text{LaMnO}_3$ ,<sup>73</sup>  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ,<sup>74</sup> and  $\text{LaCoO}_3$ <sup>75</sup> perovskites using anodic oxidation. This process involves electrochemically incorporating  $\text{La}^{3+}$  ions into metal oxyhydroxide films, followed by thermal treatment to achieve the perovskite phase. However, challenges include controlling the incorporation of  $\text{La}^{3+}$  ions and ensuring uniform phase formation.<sup>72</sup>

Cathodic reduction methods have also been employed, where metal cations are codeposited from a mixed nitrate solution, forming hydroxide precursors that convert into perovskite oxides after heat treatment. This method facilitates better control over composition and enables the synthesis of perovskites like  $\text{LaMO}_3$  ( $\text{M} = \text{Al, Mn, Fe, Co, Ni}$ ).<sup>70</sup>

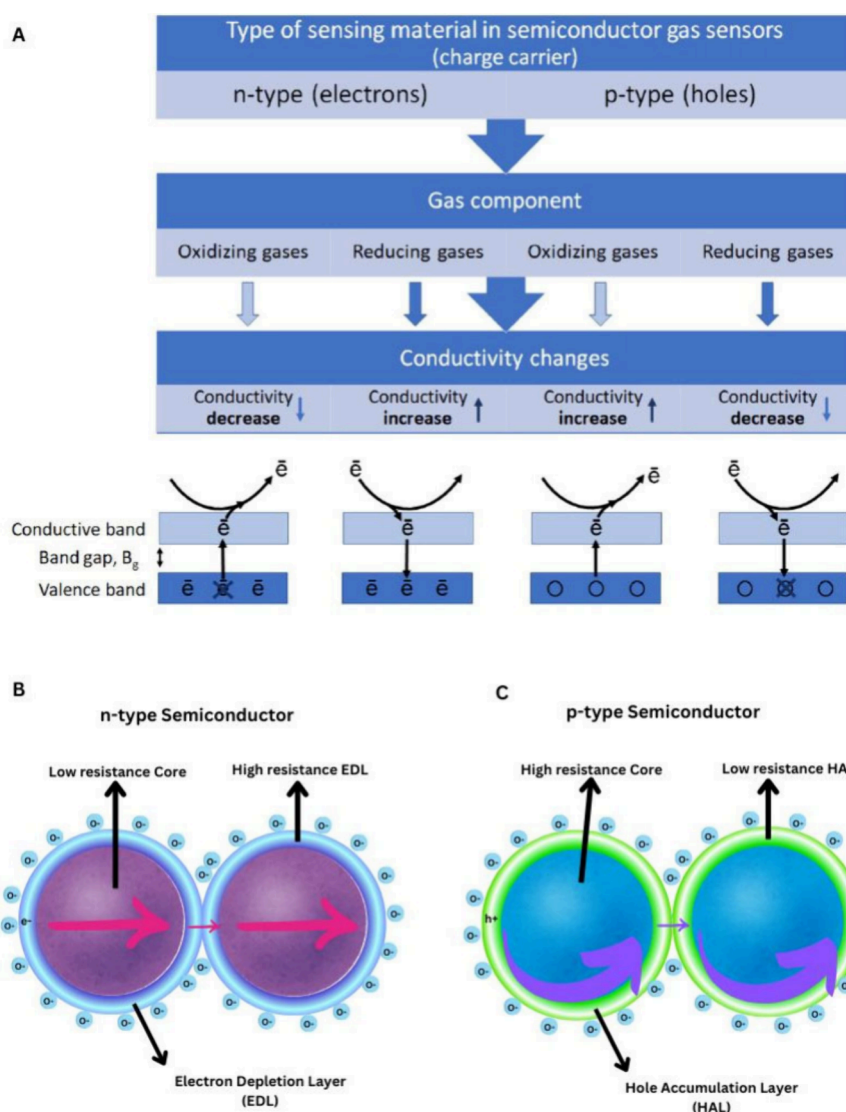
Additionally, chemically assisted electrodeposition (CAED) has been introduced as a novel technique for fabricating perovskite electrodes with a nanostructured morphology. This method combines electrodeposition with chemical precipitation, allowing the formation of highly porous, catalytically active electrodes.<sup>72</sup>

#### 4. MECHANISMS OF GAS SENSING IN PEROVSKITE-BASED SENSORS

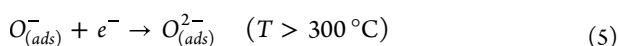
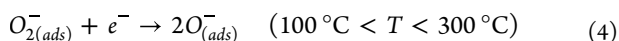
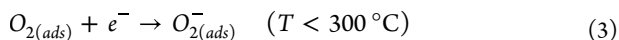
The widely recognized gas sensing mechanism for resistive-type gas sensors, including perovskite-based ones, involves changes in the material's conductivity due to the desorption and adsorption of gas molecules on the surface of the probing material when exposed to target gases (Figure 7). This mechanism is influenced by the properties of both the sensor material and the target gases.<sup>28</sup> In air, oxygen molecules adsorb onto the surface of semiconductor perovskites, where surface reactions occur between the target gases and the chemisorbed oxygen species (such as  $\text{O}^-$ ,  $\text{O}_2^-$ , and  $\text{O}^{2-}$ ). These oxygen species form by extracting surface electrons, with the specific species depending on the temperature range. The general reactions include:<sup>3,76</sup>



**Figure 7.** Schematic of the gas-sensing behavior of perovskite oxide materials.



**Figure 8.** A) Description of the gas-sensing mechanism and the conduction model toward different gases. Reproduced with permission from.<sup>26</sup> B,C) Charge carrier mechanism in different types of semiconductors.



In n-type semiconductors, where electrons are the main charge carriers, the formation of chemisorbed oxygen ions reduces the electron density, creating an electron depletion layer that raises the resistance. Conversely, in p-type semiconductors, where holes are the primary charge carriers, the adsorption of oxygen ions produces a hole accumulation layer near the surface and an insulating core, which increases conductivity by boosting hole concentration (Figure 8).

When p-type perovskites encounter reducing gases (e.g., acetone, ethanol, acetaldehyde, formaldehyde, methane, or hydrogen sulfide), the reducing gas reacts with adsorbed oxygen ions, releasing trapped electrons and neutralizing holes. This lowers the charge carrier concentration, thereby increasing the resistance. For oxidizing gases (e.g., nitrogen dioxide, hydrogen peroxide, ozone, carbon dioxide, sulfur dioxide), the interaction increases hole concentration and decreases resistance.<sup>77</sup>

In n-type perovskites, interaction with reducing gases, which typically compensate for oxygen vacancy deficiencies, results in higher electron concentration and lower resistance, as electrons are returned into the conduction band by the ionized oxygen species. In oxidizing environments, the target gas reduce by taking electrons from the conduction band, leading to the resistance of n-type perovskites increases.<sup>78,79</sup>

## 5. OPTIMIZATION OF THE GAS-SENSING PROPERTIES OF THE PEROVSKITE MATERIALS

**5.1. Tailoring the Chemical Composition of the Perovskite Materials.** Typically, perovskite oxide-based sensors with p-type properties exhibit a mechanism of resistance change that is the opposite of that of n-type semiconductor sensors, leading to a reduced response in the environment of volatile organic compounds (VOCs) or sulfuric compounds (VSCs). To overcome this limitation, many studies have focused on various strategies such as doping at the A and B sites within the perovskite structure, incorporating noble metal catalysts, and applying nanoengineering techniques to increase the surface area and porosity.



The sensing properties of  $\text{ABO}_3$  perovskites can be significantly improved by incorporating various cationic elements into the A and B sites of the structure. Doping these materials enhances their selectivity and sensitivity to volatile organic compounds (VOCs) and reduces both response and recovery times. Liu et al. doped yttrium (Y) into  $\text{LaFeO}_3$  (LFO) at different concentrations, with 0.8 mol % Y showing the highest sensing response. The incorporation of Y increases the number of free electrons and surface charge exchange, leading to more active sites for gas adsorption and stronger gas molecule interaction.<sup>80</sup> Qin et al. replaced a low-valence B-site cation with phosphorus ( $\text{P}^{5+}$ ), which substituted part of the B–O octahedra in the perovskite structure with P–O tetrahedra, creating oxygen vacancies. This doping significantly enhanced the sensor's sensitivity to acetone at 180 °C, although excessive P doping led to reduced performance due to increased resistance in the presence of acetone, a reducing gas.<sup>81</sup> Additionally, doping with magnesium ( $\text{Mg}^{2+}$ ) improved LFO's performance for methanol detection, as  $\text{Mg}^{2+}$  creates oxygen vacancies, enhancing gas sensitivity by facilitating oxygen absorption.<sup>82</sup>

Furthermore, both A-site and B-site doping have been explored for improving gas sensing in perovskites. For example, Liu et al. found that doping  $\text{Y}^{3+}$  in  $\text{LaMnO}_3$  enhanced acetone sensing by increasing the number of adsorbed oxygen species and promoting the formation of  $\text{Mn}^{4+}$  ions.<sup>83</sup> Similarly, doping calcium ( $\text{Ca}^{2+}$ ) in  $\text{GdFeO}_3$ , a p-type semiconductor, generated oxygen vacancies and promoted hole production, improving sensitivity and selectivity for methanol.<sup>84</sup>

However, there remains a considerable need for more efficient and effective processing approaches to improve the practical use of perovskite oxide-based sensors. Modifying the composition of a material, either partially or completely, can be a potential strategy to boost the gas response of p-type materials.

The role of defects in semiconductors has been extensively studied, and various techniques such as hydrothermal methods, surface engineering, and ion-beam irradiation have been used to create and understand these defects.<sup>85–89</sup> Defects, particularly voids or missing lattice sites, are significant, as they influence the sensor response. These defects, which can be shallow or deep donors depending on their energetics, impact gas sensing by altering the electrical properties of the materials. Specifically, deficiencies at the A- or B-sites and oxygen vacancies in perovskite oxide-based materials are known to influence the adsorption and dissociation energy between oxygen species and target analytes, thereby enhancing selectivity. Oxygen vacancy defects ( $\text{VO}\cdot$ ,  $\text{O}$ , and  $\text{O}^{2-}$ ) play crucial roles in gas sensor response, and the sensor's electrical resistance is influenced by the target gas's partial pressure and defect concentration.<sup>90</sup> Recently, investigation on the freeze-dried assisted sol–gel synthesized  $\text{SmFeO}_3$  revealed a superior acetylene sensing ability that related to the rich surface oxygen vacancies.<sup>91</sup>

For example, in perovskite materials, defects such as surface vacancies created during the synthesis process can lead to lower conductivity, but these can be passivated by adsorbing target vapors like ethanol. The adsorbed vapors help release trapped electrons, boosting the material's conductivity. Surface defects, which act as a route for ion diffusion, can be detrimental, leading to ion migration and reduced performance over time.<sup>92</sup>

Further, in the case of multiferroic sensors, such as  $\text{BiFeO}_3$  (BFO), defects at domain walls, including  $\text{Fe}^{4+}$  ions and Bi vacancies, impact the sensor's behavior. These defects increase the presence of adsorbed oxygen species, which can reduce response times under thermal excitation. Magnetic excitation

can further activate these adsorbed oxygen species, reducing the ideal operating temperature and speeding recovery times. This suggests that while surface defects may limit performance in optical applications, they are advantageous for humidity and gas sensing due to their ability to facilitate oxygen adsorption and charge transfer.<sup>93</sup> In conclusion, defects play a pivotal role in enhancing or hindering the performance of gas sensors, with specific defects like oxygen vacancies and surface defects contributing to improved sensitivity and faster response times when managed properly.

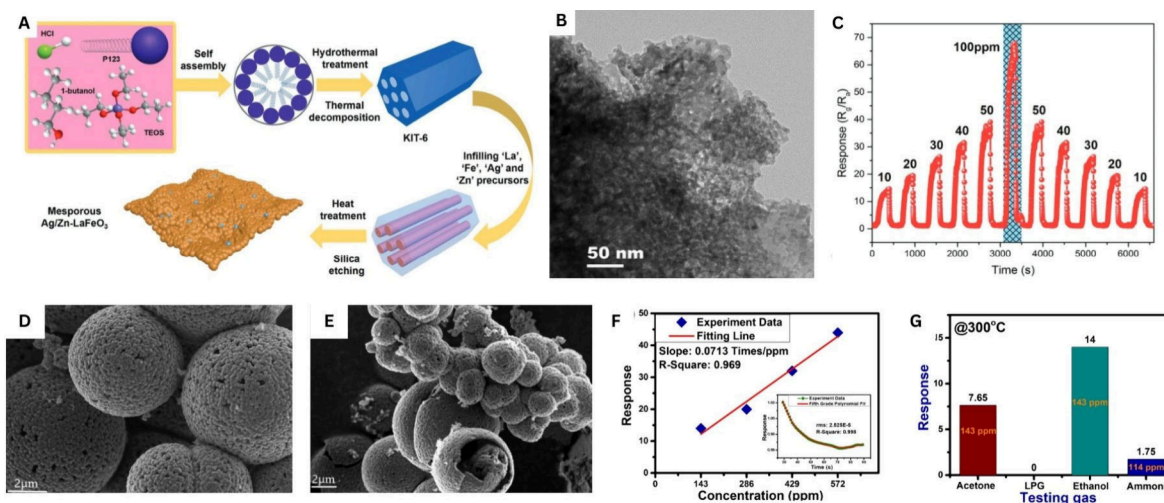
Additionally, incorporating perovskite oxide with spillover effects into the sensing layer can enhance the quantity of oxygen species, which provides higher reaction sites for molecules of the target gases.

These studies illustrate how doping and defects in  $\text{ABO}_3$  perovskites, such as the creation of oxygen vacancies and the introduction of new active sites, significantly enhance their gas sensing performance.

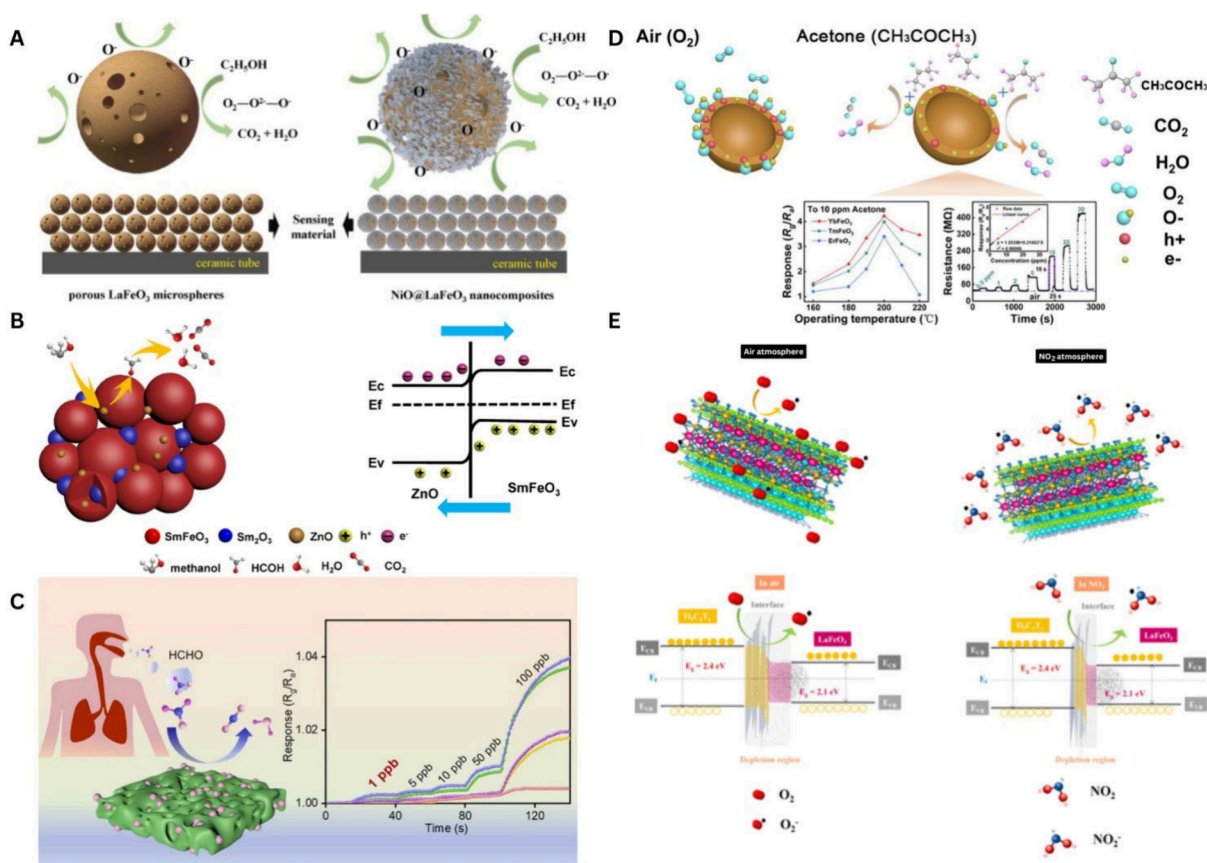
**5.2. Tuning the Morphology of the Perovskite Materials.** The morphology of materials plays a crucial role in enhancing the gas-sensing performance, especially for volatile organic compounds (VOCs) at various concentrations and temperatures. Nanomaterials, with their high surface-to-volume ratios, exhibit superior sensing effects. For thin-film-based sensors, the grain size significantly influences sensor properties, as smaller grains (less than twice the Debye length) lead to better charge transfer, improving sensitivity.<sup>94</sup> Using a porous structure with a large surface area is a widely used and effective approach to enhancing gas sensing performance. Porous materials, due to their special structural and morphological characteristics, have been extensively studied in this regard.<sup>95</sup> Among the various synthesis techniques, the template method has proven to be highly effective for producing porous materials. Recently, metal–organic frameworks (MOFs) have gained significant attention as an innovative template for fabricating porous nanomaterials.<sup>96</sup> MOFs themselves are porous, multi-functional materials composed of metal clusters interconnected by functional organic ligands.<sup>97</sup> Their exceptional features, including uniform porous structure with high surface area, make them suitable for different applications, including catalysis,<sup>98</sup> drug delivery,<sup>99</sup> gas storage, separation, and gas sensing.<sup>100</sup>

Additionally, MOFs offer a unique pathway for synthesizing porous perovskite structured nanomaterials. Modified  $\text{La}_{0.8}\text{Ca}_{0.2}\text{Fe}_{0.98}\text{Pt}_{0.02}\text{O}_3$  gas sensor using (MOF)-derived  $\alpha$ - $\text{Fe}_2\text{O}_3$  nanoparticles demonstrated exceptional chemoresistive performance for acetone detection at 250 °C.<sup>101</sup> Hollow box-shaped  $\text{CNT@ZnSnO}_3$  synthesized by a hydrothermal method and Zn-MOF (ZIF-8) exhibited excellent ethanol sensing performance due to large specific surface area.<sup>102</sup>

Materials with varying morphologies, such as nanofibers, thick films, and powders, show different gas sensing performances. For example,  $\text{LaFeO}_3$  (LFO) in the nanofiber form detected ethanol at a lower temperature but had slower response times compared to the thicker film version, which exhibited higher sensitivity despite slower recovery times. The material's surface area, pore size, and crystallite structure all influence these outcomes.<sup>103,104</sup> Phan et al. reported that  $\text{LaFeO}_3$  indicates different ethanol-sensing properties depending on the morphological structure. They have synthesized  $\text{LaFeO}_3$  with a hollow core and porous shell structure using a surfactant-assisted hydrothermal method.  $\text{LaFeO}_3$  with porous structure has shown better selectivity and higher sensitivity in comparison to a bulk structure.<sup>105</sup> A study explored hierarchically porous  $\text{LaFeO}_3$



**Figure 9.** A) Schematic diagram of the synthesis process by hard template of KIT-6, B) TEM image, and C) dynamic response of mesoporous Ag/Zn-LaNiO<sub>3</sub> nanocomposites toward ethanol gas and toward different gases. Reproduced with permission from.<sup>106</sup> D, E) SEM images and F, G) ethanol sensing performance of hollow LaNiO<sub>3</sub> toward different gases. Reproduced with permission from.<sup>105</sup>



**Figure 10.** Gas sensing properties of the perovskite materials A) ethanol gas sensor based on LaFeO<sub>3</sub> microspheres decorated with NiO nanosheets,<sup>114</sup> B) methanol gas sensor based on Sm<sub>2</sub>O<sub>3</sub>/ZnO/SmFeO<sub>3</sub> microspheres,<sup>116</sup> C) formaldehyde gas sensor based on In-doped LaFeO<sub>3</sub> porous structure,<sup>120</sup> D) acetone gas sensor based on porous YbFeO<sub>3</sub> nanocrystalline,<sup>124</sup> and E) NO<sub>2</sub> gas sensor based on cotton-modified LaFeO<sub>3</sub>/MXene composites.<sup>137</sup> All figures are reproduced with permission.

synthesized using a cost-effective and scalable method. By optimizing the quantity of the structuring agent F108 and the calcination temperature, the gas-sensing performance was significantly improved. The LaFeO<sub>3</sub> prepared with 0.5 g of F108 exhibited the best response, achieving a sensitivity of 116 to 50 ppm formaldehyde at 125 °C with a trace detection limit as low as 50 ppb. The enhanced performance was attributed to the

material's hierarchical porous structure, which provides a high surface area and large pore volume.<sup>76</sup> This approach highlights the importance of morphological tuning for achieving superior gas-sensing properties and positions LaFeO<sub>3</sub> as a promising material for accurate and noninvasive formaldehyde detection.

The mesoporous Ag/Zn-LaNiO<sub>3</sub> nanocomposite synthesized through a facile nanocasting technique using silica hard

template KIT-6 using KIT-6 in a sol–gel route is showed high sensing performance toward ethanol at the low temperature of 55 °C. This superior functionality is related to the high surface area and the catalyst behavior of  $\text{Zn}^{2+}$  at the surface of the sensing materials (Figure 9-A-C).<sup>106</sup> Phan et al. synthesized hollow  $\text{LaFeO}_3$  (LFO-HS) using a hydrothermal method, with cetyltrimethylammonium bromide (CTAB) playing a crucial role in shaping the particle morphology. The presence of CTAB resulted in a hollow, porous structure with a large surface area, enhancing the gas sensing performance. The LFO-HS-based sensor demonstrated a high resistance, making it suitable for low-power applications. Optimal performance was achieved with a 6-layer LFO-HS sensor at 300 °C, showing strong selectivity for ethanol over acetone, LPG, and ammonia. It exhibited a linear response with an ultralow ethanol detection limit of 1 ppb. Compared to bulk LFO synthesized via a solid-state reaction, the hollow structure significantly improved sensitivity due to differences in structural and microstructural properties. These findings highlight the effect of morphology in the sensing performance of  $\text{LaFeO}_3$  (Figure 9-D-G).<sup>105</sup>

## 6. GAS-SENSING PROPERTIES OF PEROVSKITE MATERIALS

**6.1. VOCs Sensing Properties.** The several hazards of the volatile organic compound (VOC) gases to human health have been studied previously;<sup>107,108</sup> also it has been shown that detection of them in human breath plays a crucial role for the early stage detection of various diseases like cancer, renal failure, etc.<sup>109–111</sup> Recently, perovskite materials have offered excellent performance for detection of VOC gases accurately, with short response/recovery time and high sensitivity and selectivity, due to their special crystalline structures and optoelectronic properties.<sup>112</sup>

Chen et al. synthesized  $\text{SmFe}_{1-x}\text{Ni}_x\text{O}_3$  nanocrystalline materials with an orthogonal perovskite structure via a sol–gel method. It was observed that increasing nickel (Ni) doping resulted in a reduced unit cell volume and average crystallite size. Sensors made from  $\text{SmFe}_{1-x}\text{Ni}_x\text{O}_3$  demonstrated improved conductivity and lower optimal working temperatures compared to  $\text{SmFeO}_3$ . At low Ni doping levels ( $x \leq 0.05$ ), the sensors exhibited enhanced sensing performance, attributed to accelerated catalytic oxidation reactions of ethanol on the surface of the material due to Ni incorporation. For example, the  $\text{SmFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$  sensor achieved a response of 57.8 to 500 ppm ethanol at 260 °C, with response and recovery times of 30 and 50 s, respectively. This improved response was associated with the smaller particle size and increased specific surface area induced by Ni doping, which facilitated the adsorption and reaction of oxygen species with ethanol, releasing electrons and enhancing resistance change. However, at higher Ni doping levels ( $x > 0.05$ ), the sensing performance declined, potentially due to the diminished role of  $\text{Fe}^{3+}$  ions at the B site, which is critical to the sensing mechanism. Additionally, Ni doping reduced the optimal operating temperature of the sensors, likely by lowering the adsorption activation energy of the material.<sup>113</sup>

Hao et al. synthesized porous  $\text{LaFeO}_3$  microspheres decorated with  $\text{NiO}$  nanosheets by using a hydrothermal method, forming a p–p heterojunction. The uniform  $\text{NiO}$  nanosheets enhanced the gas interaction surface, significantly improving ethanol sensing performance with high sensitivity, selectivity, and fast response/recovery times. The hierarchical structure and heterointerfaces facilitated oxygen adsorption, making  $\text{NiO}@\text{LaFeO}_3$  a promising material for ethanol

detection and offering valuable insights for designing advanced gas sensors (Figure 10-A).<sup>114</sup>

A recent study focused on the preparation of  $\text{LaFeO}_3/\text{In}_2\text{O}_3$  composites through hydrothermal methods and analyzed their microstructures and crystal properties. The ethanol sensitivity tests revealed that the  $\text{LaFeO}_3/\text{In}_2\text{O}_3$  composite gas sensor exhibited superior performance compared to pure  $\text{In}_2\text{O}_3$ . Further calculations and analysis using the first-principles method revealed that  $\text{LaFeO}_3$  improves the performance of the  $\text{In}_2\text{O}_3$  sensor by increasing oxygen adsorption, creating a heterojunction with unique Fermi level effects, and catalyzing redox reactions. These factors collectively contribute to the enhanced sensitivity of the  $\text{LaFeO}_3/\text{In}_2\text{O}_3$  composite sensor.<sup>115</sup>

A recent study developed an Ag-doped double perovskite  $\text{LaFe}_{1-3}\text{Sn}_x\text{O}_3$  (Ag-LFSO) nanocomposite using a sol–gel-assisted microwave chemical synthesis method. This composite demonstrated both fast response and good selectivity for methanol detection. The Ag-LFSO sensor exhibited a response of 51.94 to 5 ppm of methanol at 99 °C, which is approximately six times higher than that of the pure  $\text{LaFeO}_3$  sensor. The enhanced response and selectivity were attributed to the substitution of  $\text{Sn}^{2+}$  in the  $\text{Fe}^{3+}$  position, which altered the carrier concentration and oxygen adsorption in  $\text{LaFeO}_3$ . Additionally, the introduction of Ag doping catalyzed surface reactions and created electron defects on the material's surface, improving its electrical conductivity and oxygen adsorption capabilities.<sup>15</sup>

Li et al. developed  $\text{Sm}_2\text{O}_3/\text{ZnO}/\text{SmFeO}_3$  microspheres using a hydrothermal-microwave method for methanol sensing. The sensor, optimized at a 24 h hydrothermal time, exhibited a high response of 119.8 to 5 ppm of methanol at 195 °C, with excellent stability over 30 days in humid conditions. Even at 1 ppm, the response remained strong, demonstrating the material's potential for methanol gas detection (Figure 10-B).<sup>116</sup>

The formaldehyde sensing ability of  $\text{LaFeO}_3$  has been widely investigated. However, several disadvantages need to be improved to achieve high sensitivity, selectivity, and reduced response/recovery times. Porous Pt-decorated  $\text{LaFeO}_3$  has been synthesized that represented 2.5 times higher response, better selectivity, and shorter response/recovery times than the pristine material at the low sensing temperature of 125 °C. This improvement is attributed to the porous structure and the increased concentration of the adsorbed oxygen.<sup>117</sup>

Dash et al. have reported that a synergistic effect of reduced graphene oxide (rGO) and  $\text{LaFeO}_3$  improved the sensing properties of the  $\text{LaFeO}_3$  gas sensor. Adsorption of formaldehyde molecules was facilitated owing to the large surface area of the rGO, while  $\text{LaFeO}_3$  represented the catalytic effect for the oxidation of formaldehyde.<sup>118</sup>

Rapid detection of formaldehyde using  $\text{YFeO}_3$  has been studied by Xukeer et al. The sensor exhibited ultrafast response-recovery times of about 6.3 s/0.9 s due to a uniform hierarchical structure and high oxygen vacancies concentration.<sup>119</sup> Xiao et al. synthesized In-doped  $\text{LaFeO}_3$  via a sol–gel method to enhance formaldehyde sensing. The sensor showed a high response of 122 at 125 °C toward 100 ppm and detected concentrations as low as 1 ppb. Improved performance was attributed to increased surface area, oxygen vacancies, and lower adsorption energy, making it a promising material for real-time formaldehyde detection (Figure 10-C).<sup>120</sup>

Bing Li et al. investigated  $\text{Sm}^{3+}$ -doped  $\text{NdFeO}_3$  (Sm-NFO), synthesized via a one-step hydrothermal method, and demonstrated that  $\text{Sm}^{3+}$  doping significantly enhances the



Table 2. VOCs sensing properties of the perovskite materials

Material	Synthesize method	Target gas	Operating temp.	concentration	response	Detection limit	ref.
SmFe <sub>0.95</sub> Ni <sub>0.05</sub> O <sub>3</sub>	sol–gel citric	Ethanol	260 °C	500 ppm	57.8		113
NiO@LaFeO <sub>3</sub>	hydrothermal	Ethanol	125 °C	100 ppm	122	1 ppb	114
LaFeO <sub>3</sub> /In <sub>2</sub> O <sub>3</sub>	hydrothermal	Ethanol	220 °C	100 ppm	147	50 ppb	115
Ag-LaFe <sub>1-x</sub> Sn <sub>x</sub> O <sub>3</sub>	microwave assisted sol–gel	Methanol	99 °C	5 ppm	51.94		15
Sm <sub>2</sub> O <sub>3</sub> /ZnO/SmFeO <sub>3</sub>	hydrothermal-microwave	Methanol	195 °C	5 ppm	119.8		116
1%Pt-LaFeO <sub>3</sub>	sol–gel	Formaldehyde	125 °C	100 ppm	144	10 ppb	117
rGO-LaFeO <sub>3</sub>	sol–gel	Formaldehyde	260 °C	1 ppm	15	19 ppb	118
YFeO <sub>3</sub>	hydrothermal	Formaldehyde	Room temp.	100 ppm	318		119
1.5 at%In- LaFeO <sub>3</sub>	sol–gel	Formaldehyde	125 °C	100 ppm	122	1 ppb	120
1%Sm-NdFeO <sub>3</sub>	hydrothermal	Formaldehyde	210 °C	100 ppm	18		121
CNT/Ag-LaFeO <sub>3</sub>	microwave assisted sol–gel	Acetone	86 °C	5 ppm	59		123
YbFeO <sub>3</sub>	sol–gel	Acetone	200 °C	10 ppm	~4	500 ppb	124
10 wt % TiO <sub>2</sub> –LaFeO <sub>3</sub>	sol–gel	Acetone	144 °C	100 ppm	37.3		125
La <sub>2</sub> O <sub>3</sub> /LaFeO <sub>3</sub>	hydrothermal	Acetone	200 °C	100 ppm	41.9	500 ppb	126

material's sensitivity and selectivity for formaldehyde detection. The enhanced sensitivity was attributed to morphological changes induced by Sm<sup>3+</sup> doping, which resulted in a lamellar structure that increased the number of active sites for gas adsorption and improved gas diffusion. Furthermore, the doping process introduced oxygen vacancies and lattice defects, boosting chemisorbed oxygen concentrations and creating additional activation sites for gas sensing. The smaller ionic radius of Sm<sup>3+</sup> also narrowed the optical bandgap and enhanced electron transport by suppressing electron–hole recombination. These combined effects improved the material's selective adsorption and overall sensing performance, making Sm<sup>3+</sup> doped NdFeO<sub>3</sub> a promising candidate for formaldehyde detection.<sup>121</sup>

Molecularly imprinted polymers (MIPs) are highly selective materials for VOC sensing, as they recognize target molecules based on both their functional groups and specific shapes. MIPs are synthesized by polymerizing functional monomers and a cross-linking agent around a target molecule (template). After the template's removal, cavities matching the target's shape and functionality remain. These cavities allow MIPs to selectively rebinding the target molecule upon exposure to a gas mixture. For VOCs like ethanol, toluene, and xylene, MIPs exhibit strong selectivity and significant changes in conductivity upon target binding, making them effective for VOC detection.<sup>122</sup> Rong et al. have employed a composite of Ag-LaFeO<sub>3</sub> molecular imprinted polymers and carbon nanotubes for sensitive detection of acetone at the low operating temperature of 86 °C.<sup>123</sup>

Meng et al. studied the selection of a suitable lanthanide that can enhance the gas sensing properties of the LnFeO<sub>3</sub> gas sensors. They have mentioned that YbFeO<sub>3</sub> represented superior gas sensing ability toward acetone with a low detection limit of 500 ppb. They have concluded that the enhanced gas-sensing performance is mainly related to the low binding energy of the Yb–O bond (Figure 10-D).<sup>124</sup>

A recent study aimed to improve the acetone sensing performance of the sol–gel synthesized LaFeO<sub>3</sub> nanoparticles for breath analysis by incorporating commercial rutile TiO<sub>2</sub> nanomaterials. The TiO<sub>2</sub>–LaFeO<sub>3</sub> nanocomposites showed enhanced surface reactivity, higher specific surface areas, and more concentration of oxygen vacancy in comparison to pure LaFeO<sub>3</sub> nanoparticles. The addition of TiO<sub>2</sub> by formation of p–n heterojunctions improved the regulation of acetone molecules and carrier conduction within the nanocomposites. As a result,

the nanocomposites showed better acetone sensing performance, improved selectivity, and lower response/recovery times.<sup>125</sup>

Wu et al. have studied mesoporous p–p heterostructure composites of La<sub>2</sub>O<sub>3</sub>/LaFeO<sub>3</sub>. The in situ formation of p–p heterojunctions effectively tailors charge carrier concentrations and modifies the energy band structure, enhancing sensing performance. Additionally, the inclusion of La, known for its high catalytic activity, promotes gas sensing reactivity and generates abundant lattice oxygen defects. Consequently, the mesoporous La<sub>2</sub>O<sub>3</sub>/LaFeO<sub>3</sub>-based gas sensor exhibited high sensitivity, rapid response and recovery times (9 s/15 s to 100 ppm acetone), excellent selectivity, and a low detection limit (500 ppb) at an operating temperature of 200 °C. In contrast, the acetone sensing performance of the LaFeO<sub>3</sub>-based sensor alone was comparatively poor. This study offers a straightforward strategy to enhance the chemiresistive sensing performance of ABO<sub>3</sub> perovskites.<sup>126</sup> The results obtained for the VOCs sensing properties of the perovskite materials have been summarized in Table 2.

**6.2. CO<sub>2</sub> Sensing Properties.** Because of the weak oxidizing and reducing properties of carbon dioxide (CO<sub>2</sub>), only a limited number of materials are suitable for the development of the CO<sub>2</sub> resistive gas sensors. LaFeO<sub>3</sub> has demonstrated CO<sub>2</sub> sensing capabilities. LaFeO<sub>3</sub> nanocrystalline powders, prepared using a sol–gel method, have shown notable CO<sub>2</sub> sensing capabilities. First-principles calculations suggest that CO<sub>2</sub> molecules donate electrons to the LaFeO<sub>3</sub> surface preadsorbed with oxygen.<sup>127</sup> To improve its performance, researchers employed a Co doping strategy. They synthesized LaFeO<sub>3</sub> and LaCo<sub>0.1</sub>Fe<sub>0.9</sub>O<sub>3</sub> nanomaterials via a sol–gel method and used them as gas sensors.<sup>13</sup> The results revealed that the LaCo<sub>0.1</sub>Fe<sub>0.9</sub>O<sub>3</sub> sensor exhibited a superior CO<sub>2</sub> sensing performance compared to the LaFeO<sub>3</sub> sensor. It can detect CO<sub>2</sub> at the wide range of 25–10,000 ppm, rapid response and recovery times (6/42 s), and higher sensitivity (6.69% response to 1% of CO<sub>2</sub>) at an optimal operating temperature of 220 °C under relative humidity of 51.9%. Characterization and theoretical analysis suggested that the enhanced performance of the LaCo<sub>0.1</sub>Fe<sub>0.9</sub>O<sub>3</sub> sensor was primarily related to the increased oxygen vacancies and higher adsorption energy introduced by Co doping. Nanoparticles of La<sub>1-x</sub>FeO<sub>3-δ</sub> with A-site deficiencies were synthesized via flame spray pyrolysis (FSP) and evaluated for their CO<sub>2</sub> sensing performance in gas mixtures containing 5%–15% CO<sub>2</sub>. The results indicated that

**Table 3. CO<sub>2</sub> sensing properties of the perovskite materials**

material	Synthesize method	Operating temp.	CO <sub>2</sub> concentration	Response	ref.
LaFeO <sub>3</sub>	sol–gel	300 °C	2000 ppm	2.19	127
LaCo <sub>0.1</sub> Fe <sub>0.9</sub> O <sub>3</sub>	sol–gel	220 °C	1%	6.69%	13
La <sub>0.95</sub> FeO <sub>3-δ</sub>	flame spray pyrolysis		15%	3.38	128
BaTiO <sub>3</sub>	coprecipitation		50 ppm	63%	129
CaO–BaTiO <sub>3</sub>	solution impregnation	160 °C	1000 ppm	65%	130
Co-doped PrFeO <sub>3</sub>	sol–gel autocombustion	Room temp.	500 ppm		131

**Table 4. NO<sub>2</sub> sensing properties of the perovskite materials**

material	Synthesize method	Operating temp.	NO <sub>2</sub> concentration	Response	ref.
LnFeO <sub>3</sub>	thermal decomposition	300 °C	10 ppm		132
SmFeO <sub>3</sub>	MOF self-templated precipitation process	200 °C	200 ppb	10.2	133
GO/SrTiO <sub>3</sub>	Modified Hammer's method	100 °C	1 ppm	3.2	134
Sr–BaTiO <sub>3</sub>	hydrothermal	room temperature	1000 ppm	88	135
LaFeO <sub>3</sub>	radio frequency magnetron sputtering	room temperature	1 ppm	29.6	136

the sensor performance was strongly influenced by the degree of A-site deficiency. Among the tested compositions ( $x = 0, 0.02, 0.05, 0.07$ , and  $0.1$ ), the La<sub>0.95</sub>FeO<sub>3-δ</sub> sensor exhibited the best performance. The improved response was attributed to an increase in oxygen vacancies and the higher valence states of B-site cations induced by the A-site deficiency.<sup>128</sup>

Another perovskite material has also been studied for its CO<sub>2</sub> sensing ability. BaTiO<sub>3</sub> nanospheres, synthesized by a coprecipitate technique, showed high sensitivity and selectivity toward CO<sub>2</sub>.<sup>129</sup> A heterostructure microsensor of CaO–BaTiO<sub>3</sub> showed high sensitivity and excellent selectivity toward CO<sub>2</sub> gas at 160 °C. The exceptional sensing performance was attributed to the precisely engineered  $n$ - $n$  nanointerfaces and the optimized energy band alignment, which facilitate efficient charge transfer when exposed to CO<sub>2</sub> gas molecules, even at low concentrations.<sup>130</sup> Recently, pristine and Co-doped PrFeO<sub>3</sub> nanomaterials were synthesized via a sol–gel autocombustion route and were explored for the CO<sub>2</sub> gas sensor working at room temperature. The study indicated that the Co-doped sensor has a higher response and shorter recovery and response times.<sup>131</sup> The results obtained for CO<sub>2</sub> sensing properties of the perovskite materials have been summarized in Table 3.

**6.3. NO<sub>2</sub> Sensing Properties.** An investigation into the NO<sub>2</sub> sensing ability of perovskite-type LnFeO<sub>3</sub> (Ln = La, Nd, Sm, Gd, and Dy) powders revealed that the SmFeO<sub>3</sub> sensor exhibited the highest sensitivity.<sup>132</sup> Porous hollow microspheres of SmFeO<sub>3</sub> were synthesized using a metal–organic framework (MOF) compound as a templating precursor. Gas sensors utilizing these microspheres demonstrated exceptional chemoresistive performance for NO<sub>2</sub> detection at 200 °C. The achieved performance included high sensitivity, with a response of 10.2 at 200 ppb and a detection limit as low as 50 ppb, along with excellent selectivity and relatively fast response and recovery times of 369 and 478 s, respectively.<sup>133</sup>

A GO/SrTiO<sub>3</sub> sensing device was created by using a simple and cost-effective method. The results revealed that pristine GO sensors exhibited weaker sensing capabilities compared to those decorated with SrTiO<sub>3</sub>. Notably, the GO/SrTiO<sub>3</sub> sensor showed the highest response and sensitivity to NO<sub>2</sub>. This improvement is attributed to the SrTiO<sub>3</sub> nanoparticles, which enhance the adsorption of nitrogen dioxide and facilitate charge transfer between the GO, SrTiO<sub>3</sub>, and adsorbed NO<sub>2</sub> molecules. Additionally, the GO/SrTiO<sub>3</sub> sensors demonstrated a low

detection limit of 72 ppb for NO<sub>2</sub> and maintained stable responses even under varying humidity levels.<sup>134</sup>

The investigation of the gas sensing performance of the screen-printed thick film of Sr-doped in BaTiO<sub>3</sub> nanostructures synthesized using a hydrothermal method at low temperature showed strong response toward NO<sub>2</sub> at room temperature at 0.2 M% of Sr doping. Strontium (Sr<sup>2+</sup>) ions with smaller ionic radius replace barium (Ba<sup>2+</sup>) ions, causing significant tetragonal distortion and lattice strain. This structural change increases ionic displacement at the B site of the ABO<sub>3</sub> lattice, leading to higher polarization and dipole moments at room temperature in Sr-doped BaTiO<sub>3</sub> compared to pristine BaTiO<sub>3</sub>, which shows a maximum dielectric constant only at ~130 °C. Enhanced polarization at room temperature facilitates adsorption of NO<sub>2</sub> and NH<sub>3</sub> gases on the surface of Sr-doped BaTiO<sub>3</sub> nanomaterials. Conversely, as polarization diminishes at higher temperatures, gas adsorption decreases.<sup>135</sup>

NO<sub>2</sub> sensing properties of the LaFeO<sub>3</sub> synthesized on a silicon substrate using the radio frequency magnetron sputtering technique revealed that nanocubes of LaFeO<sub>3</sub> exhibited good performance toward 1 ppm of NO<sub>2</sub> gas at room temperature. This remarkable performance is attributed to their porous structure, morphology of the surface, high surface-active sites, and the high concentration of oxygen vacancies.<sup>136</sup> Dhariwal et al. developed a room-temperature NO<sub>2</sub> gas sensor using a cotton-modified LaFeO<sub>3</sub> (CLFO) composite combined with MXene. The CLFO/MXene sensor, synthesized via a hydrothermal method, exhibited p-type behavior and excellent recoverability, achieving a 14.2-fold higher response at 5 ppm of NO<sub>2</sub>. It demonstrated a rapid response time of 2.7 s, a recovery time of 6.2 s, and strong stability. The enhanced sensitivity was attributed to surface gas interactions, adsorption energy, and charge transfer mechanisms (Figure 10-C).<sup>137</sup> The results obtained for NO<sub>2</sub> sensing properties of the perovskite materials have been summarized in Table 4.

## 7. CHALLENGES AND FUTURE TRENDS

Despite significant advancements in perovskite oxide-based gas sensors, several challenges persist, limiting their practical applications. One of the most important issues is the effect of environmental factors such as humidity and temperature variations on sensor performance. High relative humidity often increases cross-sensitivity and reduces selectivity,<sup>138,139</sup>

while temperature changes can destabilize oxygen vacancies and alter adsorption mechanisms, leading to unstable responses.<sup>140</sup> Additionally, the long-term stability of perovskite-based sensors remains a concern, as prolonged exposure to reactive gases or harsh conditions can degrade material properties, impacting performance and reliability. The scalability of synthesis techniques also presents challenges, particularly for complex morphologies or nanostructures that require precise control, making large-scale production expensive and time-consuming.

Addressing these limitations requires innovative approaches. For example, developing humidity-tolerant materials through surface functionalization or hydrophobic coatings could reduce the cross-sensitivity problem. Enhancing the thermal stability of perovskite structures via doping or composite formation may improve their stability at varying temperatures. Moreover, utilization of advanced fabrication techniques, such as additive manufacturing (3D printing) or roll-to-roll processing, could enable the scalable production of nanostructured perovskite sensors at reduced costs. Using machine learning and computational modeling to predict optimal material compositions and morphologies for specific gases can accelerate the discovery of high-performance sensors.

Future trends in this field are likely to focus on multifunctional sensors capable of detecting multiple gases simultaneously with high selectivity and sensitivity. Additionally, the use of perovskite sensors in Internet of Things (IoT) platforms for real-time environmental monitoring can be useful. These smart systems could provide continuous feedback on air quality with applications ranging from industrial emission monitoring to indoor air purification. By addressing current challenges and embracing these emerging trends, perovskite oxide-based sensors can result in highly efficient, scalable, and useful tools for environmental and industrial applications.

## 8. CONCLUSION

Perovskite oxide-based materials have emerged as efficient materials for gas sensing, offering customizable structural and functional properties. Recent advances, such as tailored doping, morphological engineering, and the creation of heterojunctions, have significantly enhanced their performance metrics. The ability to tune oxygen vacancies, modulate band structures, and integrate catalytic elements has enabled superior sensitivity and selectivity toward critical gases such as VOCs, NO<sub>2</sub>, and CO<sub>2</sub>. Despite these advances, challenges such as humidity interference, long-term stability, and cost-effective scalability exist and need further research. Future research should focus on optimizing synthesis techniques, exploring novel dopants, and using advanced computational methods to predict and enhance material behavior. By addressing these challenges, perovskite materials can fully realize their potential as efficient and scalable solutions for diverse gas-sensing applications.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

No data was used for the research described in the article.

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## Notes

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