

# Recent Trends in Binary Metal Oxides for Gas Sensing Applications and Future Opportunities: A Brief Review

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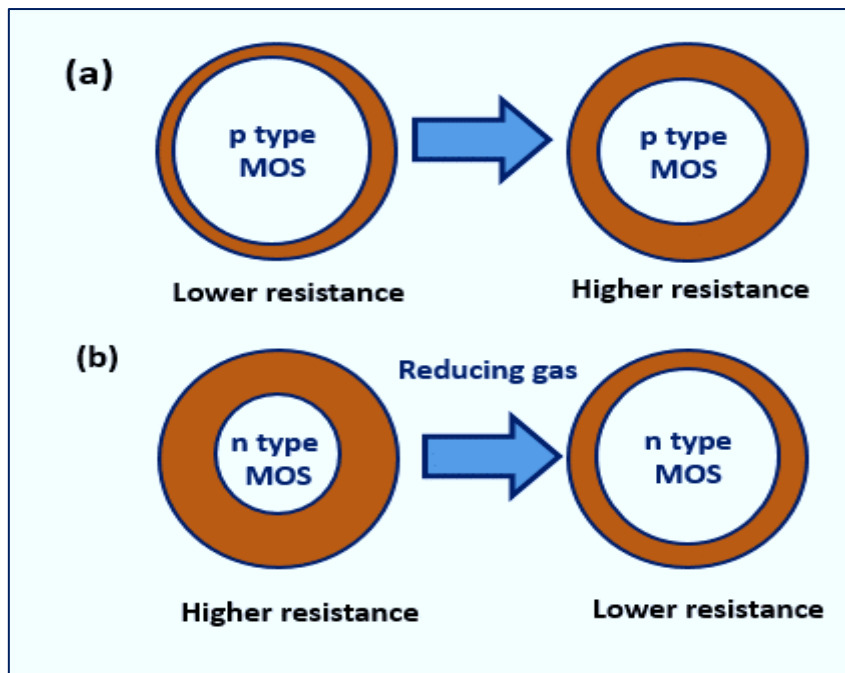
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**Abstract:** Binary metal oxides (BMOs) have emerged as a pivotal class of materials in the field of gas sensing due to their distinct physicochemical properties, including high surface reactivity, tunable band gaps, and robust thermal stability. This paper provides a comprehensive review of recent trends in the development of BMO-based gas sensors, with a focus on advancements in material synthesis, nanostructuring, and surface modification techniques. The role of various BMOs, such as ZnO, SnO<sub>2</sub>, TiO<sub>2</sub>, MnO<sub>2</sub> and TiO<sub>2</sub>, is explored in the context of their sensitivity, selectivity, and response times for detecting hazardous gases like oxidizing and reducing gases. Key challenges, such as the trade-offs between sensitivity and stability, and the limitations in operating temperatures, are also discussed. Furthermore, the paper delves into future opportunities, emphasizing the potential of hybrid BMO composites, integration with advanced nanomaterials and the development of flexible, wearable sensors.

**Keywords:** Binary metal oxides, band gaps, synthesis, surface modification, hazardous gases.

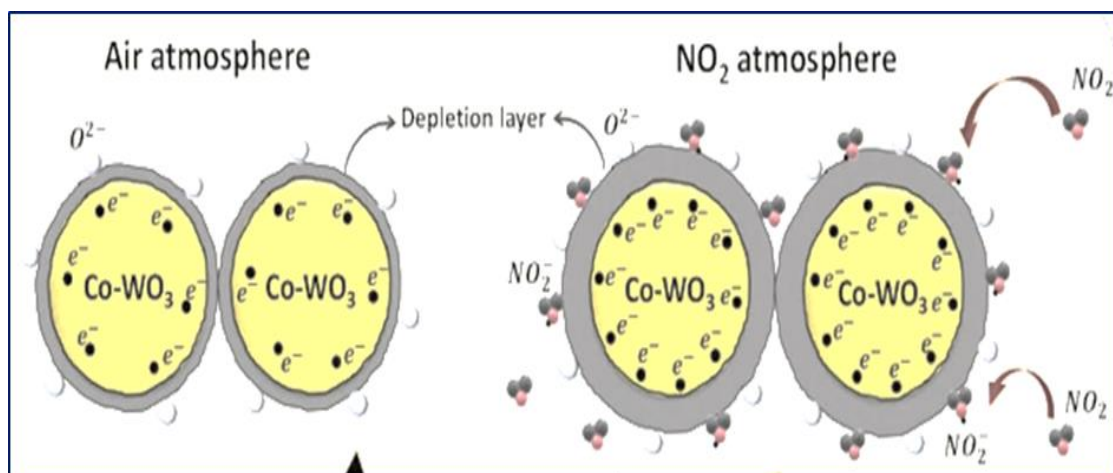
## 1. Introduction:

The increasing demand for precise and reliable gas detection across various sectors has underscored the need for novel gas sensors that surpass the limitations of traditional technologies [1, 2]. Gas sensors play a key role in a wide range of applications, from environmental monitoring and industrial safety to healthcare diagnostics and homeland security [2, 3]. Pure metal oxides such as n-type and p-type have been widely used in gas sensing applications due to their high sensitivity, they also suffer from several inherent limitations [4]. One major drawback is their lack of selectivity; pure metal oxides often respond to multiple gases, leading to cross-sensitivity issues that compromise the accuracy of detection. Additionally, these sensors typically require high operating temperatures to achieve optimal performance, which increases power consumption and limits their use in portable or wearable devices [4, 5]. The long-term stability of pure metal oxide sensors is also a concern, as prolonged exposure to harsh environments can lead to degradation and drift in sensor signals. Moreover, the response and recovery times of these sensors also slow, particularly when detecting gases at low concentrations [6, 7]. These limitations highlight the need for further research into material modifications, such as doping, hybridization, or the incorporation of nanostructures, to enhance the performance and reliability of metal oxide-based gas sensors [8, 9]. The gas sensing working principle of metal oxide semiconductors (MOS) are based on the change in resistance of the material or film as shown in Fig. 1. In presence of air generally the resistance of p type MOS is lower and when the reducing gas like H<sub>2</sub>S, NH<sub>3</sub> are kept in contact with p type MOS then resistance is increases as shown in Fig. 1 (a).



**Fig. 1.** Change in resistance of MOS in presence of reducing gas

Among the various materials explored for gas sensing, binary metal oxides (BMOs) have garnered significant attention due to their unique combination of chemical and physical properties. BMOs, composed of two metal elements, offer a versatile platform for tailoring sensor performance through adjustments in composition, morphology, and surface chemistry. Recent years have witnessed substantial progress in the synthesis of BMOs with nanostructured features, leading to enhanced surface areas and improved gas-sensing capabilities [10-13]. However, the performance of BMO-based sensors is often influenced by factors such as operating temperature, humidity, and cross-sensitivity to other gases, posing challenges in achieving reliable and selective gas detection. Fig. 2 reveals the BMO gas sensing mechanism in presence of  $\text{NO}_2$  gas.



**Fig. 2.** BMO gas sensing mechanism in presence of  $\text{NO}_2$  gas.

In material synthesis, methods such as sol-gel processing, hydrothermal synthesis, and chemical vapor deposition have been refined to achieve precise control over the composition and phase of BMOs, enabling the development of materials with enhanced sensing properties. For instance, sol-gel techniques have facilitated the creation of uniform and homogeneous BMO coatings, while hydrothermal methods have enabled the growth of well-defined nanostructures [13, 14]. Nanostructuring techniques, including electrospinning, template-assisted synthesis, and atomic layer deposition, have advanced the fabrication of BMO-based materials with tailored nanomorphologies. These nanostructures such as nanoparticles, nanowires, and nanosheets offer increased surface area and active sites, which enhance the sensitivity and response speed of gas sensors [13 -15].

Surface modification techniques have also played a crucial role in optimizing the performance of BMO-based sensors. Doping with various elements, such as noble metals or non-metals, has been shown to alter the electronic and catalytic properties of BMOs, enhancing their sensitivity and selectivity towards specific gases. Additionally, functionalization with organic compounds or nanoparticles can improve the interaction between the sensor surface and target gases, further refining sensor performance [16, 17]. Hybridization with materials like graphene or carbon nanotubes has been explored to combine the strengths of different materials, resulting in sensors with superior electrical conductivity and enhanced performance.

This paper aims to review the latest advancements in BMO gas sensors, highlighting emerging trends in material design, functionalization strategies, and sensor integration. Additionally, it explores the potential of combining BMOs with other nanomaterials and advanced technologies to overcome existing limitations and expose new opportunities for the next generation of gas sensing devices.

## 2. Literature survey

The field of gas sensing has seen significant advancements in recent years, with BMOs emerging as a promising class of materials due to their tunable properties and enhanced performance characteristics. Numerous studies have highlighted the superior gas sensing performance of ZnO-SnO<sub>2</sub> composites, particularly for detecting reducing gases like H<sub>2</sub> and CO. Park et al. (2020) demonstrated that ZnO-SnO<sub>2</sub> nanostructures exhibited higher sensitivity and faster response times compared to their single-component counterparts, attributed to the synergistic effects of the combined materials [18, 19]. Zhang et al. (2021) reported that the heterojunctions formed between ZnO and SnO<sub>2</sub> in their nanocomposite sensors significantly improved selectivity and reduced operating temperatures. Another area of active research is the development of CuO-ZnO nanostructures, which have shown excellent potential for detecting volatile organic compounds (VOCs) and toxic gases like NO<sub>2</sub> [20, 21]. Li et al. (2022) studied CuO-ZnO nanorods and found that the presence of CuO not only enhanced the surface reactivity but also reduced the operating temperature, making the sensors more energy-efficient. The combination of p-type CuO with n-type ZnO creates a p-n heterojunction, which plays a crucial role in improving sensor response and recovery times [21, 22]. Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> binary oxides have also attracted attention due to their high sensitivity to gases such as ethanol and ammonia. According to a study by Kumar et al. (2023), Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanocomposites showed a remarkable enhancement in gas sensing performance due to the increased surface area and the formation of active sites that facilitate gas adsorption and reaction [23, 24]. Additionally, the researchers observed that doping with noble metals like Pt or Au further improved the sensor's selectivity and reduced the effects of humidity on performance. CuO-SnO<sub>2</sub> composites have garnered considerable attention in recent years as a promising material for gas sensing applications, owing to their synergistic properties that enhance sensitivity, selectivity, and stability. The combination of p-type CuO and n-type SnO<sub>2</sub> forms a p-n heterojunction, which plays a crucial role in modulating the electrical properties of the composite and improving gas sensing performance [25]. Initial studies on CuO-SnO<sub>2</sub> composites focused on understanding the basic interactions between the two oxides. Choudhury et al. (2016) demonstrated that the formation of CuO-SnO<sub>2</sub> heterojunctions led to a significant improvement in gas sensing performance, particularly for reducing gases like CO and H<sub>2</sub>. The p-n junction created at the interface of CuO and SnO<sub>2</sub> facilitates charge carrier separation, leading to a more pronounced change in resistance upon gas exposure, which is critical for achieving high sensitivity. The evolution of nanostructuring techniques has further enhanced the gas sensing capabilities of CuO-SnO<sub>2</sub> composites. Wang et al. (2018) synthesized CuO-SnO<sub>2</sub> nanofibers using electrospinning, which exhibited superior sensitivity and faster response times compared to bulk composites. The increased surface area and active sites provided by the nanofiber structure contributed to the improved performance. Similarly, Patel et al. (2019) reported that CuO-SnO<sub>2</sub> nanowires demonstrated excellent selectivity towards H<sub>2</sub>S gas, with a low detection limit, attributed to the unique one-dimensional structure that enhances gas diffusion and adsorption [25, 26]. Recent studies have explored the role of doping and surface functionalization in further enhancing the gas sensing properties of CuO-SnO<sub>2</sub> composites. Zhang et al. (2020) investigated the effects of Ag doping on CuO-SnO<sub>2</sub> nanocomposites and found that Ag nanoparticles significantly improved the selectivity and response speed of the sensor, particularly for ethanol detection. The presence of Ag facilitated the catalytic decomposition of ethanol, enhancing the sensor's performance. Another study by Liu et al. (2021) explored

surface functionalization with graphene oxide, which provided additional pathways for electron transfer and improved the overall sensitivity of the sensor to NO<sub>2</sub> gas.

La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composites have emerged as a promising material in the field of gas sensing due to their unique combination of properties, which include high catalytic activity, stability, and tunable electronic structure. The integration of lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), a rare earth oxide with strong basicity, with titanium dioxide (TiO<sub>2</sub>), a well-known n-type semiconductor, creates a composite with enhanced gas sensing capabilities. Early studies focused on understanding the interaction between La<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> and how this combination affects gas sensing properties. Lee et al. (2015) demonstrated that the introduction of La<sub>2</sub>O<sub>3</sub> into TiO<sub>2</sub> significantly improved the sensor's sensitivity to reducing gases like hydrogen (H<sub>2</sub>) and carbon monoxide [27]. The enhancement was attributed to the increased oxygen vacancy concentration at the La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> interface, which facilitated greater adsorption and reaction with gas molecules. Advances in synthesis techniques have led to the development of La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composites with various nanostructures, such as nanoparticles, nanorods, and thin films, which exhibit improved gas sensing performance. Kim et al. (2018) synthesized La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanorods through a hydrothermal method and observed that these nanorods showed superior sensitivity and faster response times to ammonia (NH<sub>3</sub>) compared to pure TiO<sub>2</sub> sensors. The one-dimensional nanorod structure provided a higher surface area and more active sites for gas adsorption, which enhanced the sensor's performance. Recent research has explored the doping of La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composites with other elements to further improve their gas sensing characteristics. For example, Sharma et al. (2020) studied the effect of doping La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composites with transition metals like cobalt (Co) and found that the doped composites exhibited higher selectivity towards nitrogen dioxide (NO<sub>2</sub>) gas. The presence of Co enhanced the catalytic activity of the sensor, leading to more efficient gas detection. Another approach investigated by Wang et al. (2021) involved surface functionalization with noble metals like palladium (Pd), which significantly improved the sensor's response to hydrogen due to the spillover effect and increased catalytic activity [28, 29].

TiO<sub>2</sub>-LaCrO<sub>3</sub> composites have attracted significant attention in the field of gas sensing due to the complementary properties of titanium dioxide and lanthanum chromite (LaCrO<sub>3</sub>). TiO<sub>2</sub> is a widely used n-type semiconductor known for its high surface area, stability, and strong oxidizing power, while LaCrO<sub>3</sub> is a perovskite-type oxide that exhibits p-type conductivity and excellent thermal stability. The combination of these materials creates a p-n heterojunction that enhances gas sensing performance by improving sensitivity, selectivity, and stability. The initial research on TiO<sub>2</sub>-LaCrO<sub>3</sub> composites focused on understanding the interaction between the two oxides and their impact on gas sensing. Sun et al. (2014) demonstrated that the integration of LaCrO<sub>3</sub> with TiO<sub>2</sub> significantly improved the sensor's response to reducing gases such as hydrogen (H<sub>2</sub>) and carbon monoxide (CO). The formation of a p-n heterojunction at the interface of TiO<sub>2</sub> and LaCrO<sub>3</sub> was found to facilitate charge carrier separation, leading to a more pronounced change in electrical resistance upon gas exposure, which is crucial for achieving high sensitivity. The development of nanostructured TiO<sub>2</sub>-LaCrO<sub>3</sub> composites has been a key area of research, with various synthesis methods being employed to enhance the surface area and gas sensing properties. Liu et al. (2017) reported the synthesis of TiO<sub>2</sub>-LaCrO<sub>3</sub> nanoparticles using a sol-gel method, which showed enhanced sensitivity to NO<sub>2</sub> gas at lower temperatures compared to pure TiO<sub>2</sub> sensors [30, 31]. The improved performance was attributed to the increased surface area and the synergistic effect of the TiO<sub>2</sub>-LaCrO<sub>3</sub> interface. Similarly, Zhang et al. (2018) explored the use of TiO<sub>2</sub>-LaCrO<sub>3</sub> nanofibers fabricated through electrospinning, which exhibited faster response and recovery times for the detection of volatile organic compounds (VOCs) such as ethanol and acetone. Recent studies have explored the doping of TiO<sub>2</sub>-LaCrO<sub>3</sub> composites with various elements to further enhance their gas sensing capabilities. For example, Jiang et al. (2019) investigated the effect of doping the composite with palladium (Pd) nanoparticles, which significantly improved the sensor's selectivity and response speed towards methane (CH<sub>4</sub>) detection. The Pd doping not only enhanced the catalytic activity but also facilitated the adsorption and dissociation of gas molecules, leading to more efficient gas sensing. Another study by Wang et al. (2020) examined the impact of adding graphene oxide (GO) to the TiO<sub>2</sub>-LaCrO<sub>3</sub> composite, which resulted in improved electrical conductivity and a lower operating temperature for the sensor [30 -33].

Manganese dioxide (MnO<sub>2</sub>) and tungsten trioxide (WO<sub>3</sub>) are both well-known metal oxides with distinct properties that make them suitable for gas sensing applications. MnO<sub>2</sub> is recognized for its strong catalytic activity and ability to promote redox reactions, while WO<sub>3</sub> is a widely studied n-type semiconductor

with excellent sensitivity to various gases, particularly nitrogen dioxide ( $\text{NO}_2$ ) and ozone [34, 35]. The combination of these two materials into  $\text{MnO}_2\text{-WO}_3$  composites has emerged as a promising approach to enhance gas sensing performance by leveraging the synergistic effects of both oxides. Early research on  $\text{MnO}_2\text{-WO}_3$  composites primarily focused on understanding the interactions between these oxides and their impact on gas sensing properties. Xu et al. (2015) demonstrated that  $\text{MnO}_2\text{-WO}_3$  composites exhibited improved sensitivity and selectivity towards  $\text{NO}_2$  compared to pure  $\text{WO}_3$  sensors. The presence of  $\text{MnO}_2$  was found to enhance the catalytic activity, promoting the adsorption and reaction of  $\text{NO}_2$  on the sensor's surface, leading to a more significant change in electrical resistance [32, 36]. Advances in nanostructuring techniques have played a crucial role in enhancing the gas sensing capabilities of  $\text{MnO}_2\text{-WO}_3$  composites. Zhang et al. (2017) synthesized  $\text{MnO}_2\text{-WO}_3$  nanowires using a hydrothermal method and reported superior sensitivity and faster response times for detecting ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) compared to their bulk counterparts. The one-dimensional structure of the nanowires provided a high surface area and facilitated gas diffusion, which improved the overall sensor performance. Similarly, Liu et al. (2018) explored the use of  $\text{MnO}_2\text{-WO}_3$  nanosheets and found that their large surface-to-volume ratio significantly enhanced the detection of low concentrations of hydrogen sulfide ( $\text{H}_2\text{S}$ ). To further improve the performance of  $\text{MnO}_2\text{-WO}_3$  composites, researchers have investigated doping with various elements and hybridization with other materials [35, 37]. Huang et al. (2019) studied the effect of doping  $\text{MnO}_2\text{-WO}_3$  composites with silver (Ag) nanoparticles. The Ag-doped composites showed enhanced sensitivity and selectivity towards ammonia ( $\text{NH}_3$ ), with a lower detection limit and faster response time. The Ag nanoparticles acted as active sites for gas adsorption and promoted the catalytic decomposition of  $\text{NH}_3$ . Another approach explored by Chen et al. (2020) involved hybridizing  $\text{MnO}_2\text{-WO}_3$  with reduced graphene oxide (rGO), which improved the sensor's electrical conductivity and allowed for gas detection at lower operating temperatures [38, 39].

Initial studies on  $\text{SnO}_2\text{-WO}_3$  composites focused on understanding the interaction between these two metal oxides and how their combination affects gas sensing properties. Xu et al. (2013) reported that  $\text{SnO}_2\text{-WO}_3$  composites exhibited enhanced sensitivity to  $\text{NO}_2$  compared to pure  $\text{SnO}_2$  and  $\text{WO}_3$  sensors. The formation of heterojunctions at the  $\text{SnO}_2\text{-WO}_3$  interface was found to facilitate charge transfer and separation, leading to a more pronounced change in resistance upon gas exposure [12, 26]. The development of nanostructured  $\text{SnO}_2\text{-WO}_3$  composites has been a significant focus, as nanostructuring provides a higher surface area and more active sites for gas adsorption. Wang et al. (2016) synthesized  $\text{SnO}_2\text{-WO}_3$  nanofibers using an electrospinning technique and demonstrated that these nanofibers showed superior sensitivity and faster response times for detecting ammonia ( $\text{NH}_3$ ) compared to bulk composites. The high aspect ratio of the nanofibers enhanced gas diffusion and interaction with the sensing material. Similarly, Li et al. (2017) investigated  $\text{SnO}_2\text{-WO}_3$  nanowires and found that their one-dimensional structure provided excellent sensitivity to ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) and acetone ( $\text{C}_3\text{H}_6\text{O}$ ), with low detection limits and fast recovery times. Recent studies have explored doping  $\text{SnO}_2\text{-WO}_3$  composites with various elements to further enhance their gas sensing capabilities. For instance, Zhang et al. (2018) investigated the doping of  $\text{SnO}_2\text{-WO}_3$  composites with palladium (Pd) and found that Pd doping significantly improved the selectivity and response speed towards methane [25-27]. The Pd nanoparticles acted as active catalytic sites, promoting the dissociation of  $\text{CH}_4$  and enhancing the sensor's performance. Another study by Huang et al. (2019) focused on functionalizing  $\text{SnO}_2\text{-WO}_3$  composites with graphene oxide (GO), which increased the composite's electrical conductivity and allowed for room temperature gas detection, particularly for  $\text{NO}_2$  [40, 41].

### 3. Future opportunities of binary metal oxides for gas sensing applications:

The future of binary metal oxides in gas sensing applications holds exciting prospects driven by advancements in material science and technology. As researchers continue to explore novel synthesis methods and material combinations, there are several key opportunities for enhancing the performance and versatility of BMO-based sensors. One significant avenue is the development of hybrid materials that combine BMOs with advanced nanomaterials, such as graphene, carbon nanotubes, or metal-organic frameworks, to create composites with superior sensitivity, selectivity, and stability. Additionally, integrating BMOs with emerging technologies, such as machine learning algorithms and smart sensor networks, promises to enhance data interpretation and enable real-time monitoring in complex environments. The miniaturization of sensors, coupled with advancements in flexible and wearable electronics, will also expand the applications of BMOs to portable and wearable devices for personal safety and health monitoring. Furthermore, there is potential for

optimizing BMOs for low-power, room-temperature operation, which could significantly broaden their use in energy-efficient and cost-effective gas sensing solutions. As these opportunities are explored, BMOs are likely to play a crucial role in addressing global challenges related to environmental monitoring, industrial safety, and public health.

#### 4. Conclusion and Future Directions:

This literature indicates that binary metal oxides are a versatile and highly effective class of materials for gas sensing applications. Continued research into novel BMO composites, nanostructuring techniques, and hybrid systems is expected to drive further improvements in sensor performance, opening up new possibilities for their use in diverse applications. Despite these advances, challenges remain in the development of BMO-based gas sensors, particularly in terms of achieving long-term stability, reducing cross-sensitivity, and lowering the operating temperature without compromising performance. Recent studies suggest that integrating BMOs with other advanced materials, such as graphene or conducting polymers, could address these challenges by enhancing the electrical and catalytic properties of the sensors. Moreover, there is a growing interest in utilizing machine learning algorithms to optimize sensor design and improve the accuracy of gas detection.

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#### Conflicts of Interest:

The author declare no conflict of interest.

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