

Engineering Opposing Response Evolution in ZnWO_4 – WO_3 Sensor Pair for Deterministic Decoding of NO_2 in Reducing Gas

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Summary:

The selective detection of NO_2 in a multicomponent gas environment is still limited by the cross-sensitivity of metal oxide sensors. In this study, a ZnWO_4 – WO_3 sensor pair is created by deliberately using opposing response trends under identical gas circumstances. In the presence of reducing gases such as CH_4 and CO , the reaction rate of ZnWO_4 decreases steadily. WO_3 has a significantly higher reaction rate than pure NO_2 , sometimes up to 3 times higher, depending on the interferent concentration. This contrast provides a structured response space in which the same NO_2 concentration generates different responses depending on the background gas combination. The distinction makes the dataset ideal for deterministic discrimination and for machine learning algorithms for classification and concentration estimation.

Keywords: Metal oxide sensors, NO_2 sensing, gas mixtures, cross-sensitivity engineering, sensor arrays, machine learning-assisted sensing

Background, Motivation and Objective

Metal oxide semiconductor sensors are widely used for detecting harmful gases due to their high sensitivity and scalability [1]. However, in a multi-component context, their selectivity decreases. In the presence of both oxidizing and reducing gases, they compete for surface reactions, leading to nonlinear responses that are difficult to interpret [2]. Most existing techniques aim to improve selectivity by adding more materials or increasing the number of sensor arrays, but this quickly increases costs and complexity. Here, we adopt a different method. We do not aim to conceal cross-sensitivity; rather, we use it on purpose [3]. By choosing materials with opposing response qualities, we can achieve complementary behavior. The goal is to show that this divergence can be employed as a reliable sensing parameter rather than as a constraint.

Description of the New Method or System

The WO_3 and ZnWO_4 thin films were prepared by DC and RF sputtering and then thermally annealed to improve their crystallinity and surface activity. Both sensors were operated simultaneously under the same conditions and exposed to NO_2 concentrations of 5 to 100 ppm in the presence of CH_4 (10–30 ppm) and CO (25–75 ppm). The two materials react with gases in very different ways. WO_3 is sensitized by vacancy-mediated sensitization in reducing

environments, thereby facilitating NO_2 adsorption and improving its response. In contrast, ZnWO_4 is dominated by electron compensation and competitive adsorption, resulting in a quenched signal. The difference creates a non-collinear two-dimensional sensing space without additional hardware, effectively encoding information about the gas mixture [4].

Results

The ZnWO_4 – WO_3 pair exhibits quite different response behavior under the same gas conditions. ZnWO_4 showed strong suppression of both CH_4 and CO (Fig. 1a and 1b), especially at low NO_2 levels. The response could drop by orders of magnitude, but it could recover at higher concentrations. In WO_3 , the opposite trend is seen. Its response increases across all mixed-gas conditions, surpassing the pure NO_2 signal and reaching much higher values, especially in CO -rich environments (Fig. 1c and 1d). The strength of this effect depends on the type and amount of the interfering gas. For example, CO has a stronger, non-monotonic effect than CH_4 . Consequently, the response ratio $R(\text{ZnWO}_4)/R(\text{WO}_3)$ is inverted and exceeds one in pure NO_2 , while it is significantly less than one in mixed conditions.

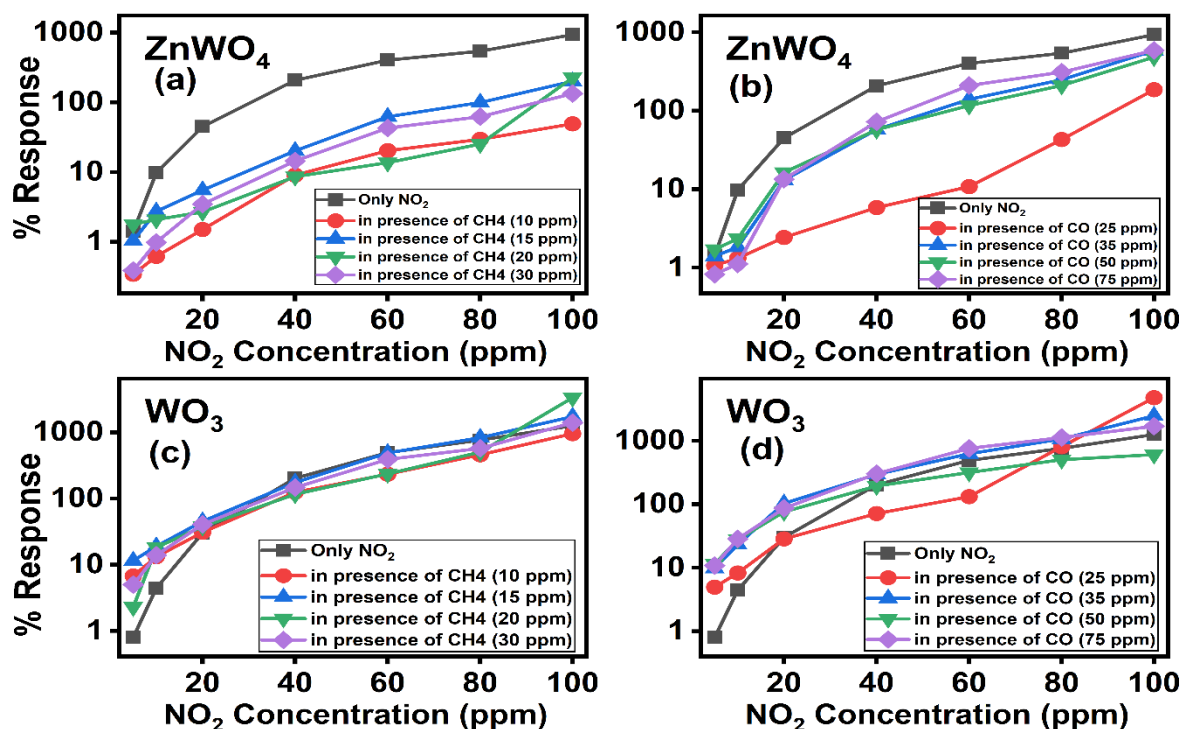


Figure 1: Percentage response as a function of NO_2 concentration for ZnWO_4 (a, b) and WO_3 (c, d) thin-film sensors under pure NO_2 and binary gas mixtures with CH_4 (a, c; 10–30 ppm fixed) and CO (b, d; 25–75 ppm fixed).

This makes a response space that is both organized and separate. It is possible to distinguish between gas identity and background concentration using the paired outputs. ZnWO_4 always shows a lower response than the pure- NO_2 baseline, while WO_3 always shows a higher response than the pure- NO_2 baseline at all levels of the interferent tested. This change occurs across the entire 5–100 ppm NO_2 range. The two-dimensional response space comprises the two opposing trends. It contains information about both the target gas and the interfering components, enabling reliable measurement of NO_2 in complex mixtures.

Conclusion

The results show that cross-sensitivity can be used positively rather than seen as a problem. The ZnWO_4 – WO_3 sensor pair lets you decode NO_2 in multicomponent environments without complicating the system by using materials that react differently. This provides a feasible pathway for developing scalable, data-driven gas sensing systems.

References

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