

Manganese Spinels Boost Gas Sensitivity in Humid Environments

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Summary:

In gas sensing, several challenges must be addressed for practical applications, particularly the presence of humidity, which has attracted significant attention. Here, we present manganese-based spinels that can leverage humidity to enhance gas sensitivity.

Keywords: Manganese, Spinel, Flame Spray Pyrolysis, Sensitivity, Humidity

Background

Humidity is a critical challenge for metal oxide (MO_x), based sensing materials, which can detect a wide range of gases and volatile organic compounds (VOCs) [1]. Various strategies have been developed to mitigate this undesired effect, including metal-functionalized MO_x , heterojunctions, and ternary oxides such as perovskite and spinel structures [2]. Here, we demonstrate that *p*-type Manganese spinels exhibit a boost on sensitivity under humid conditions for acetone detection.

Experimental

Manganese spinels-based sensing films were fabricated by flame spray pyrolysis (FSP) [3]. The precursor solutions based on Mn (II) 2-ethylhexanoate and/or Zn (II) 2-ethylhexanoate in xylene were atomized and combusted. Nanoparticles were collected on a filter positioned above the flame. The manganese oxide nanoparticles were directly deposited onto Al_2O_3 substrates with interdigitated Pt electrodes and a resistance temperature detector and annealed at 500 °C for 5 h [4]. Fig. 1 shows the fabrication of nanoparticles and sensing films by FSP. The sensors were mounted on specific holders and connected to a gas mixing system for analysis, using hydrocarbon-free synthetic air and calibrated mass flow controllers to create the desired gas mixture composition [5]. The sensor response (*S*) was established as follows:

$$S = R_g/R_a - 1 \quad (1)$$

Results

The synthesized materials by the FSP were MnO_x (90 mol% Mn_3O_4 and 10 mol% Mn_2O_3) and ZnMn_2O_4 spinels, which were characterized by X-ray diffraction (XRD), specific surface area (SSA) via the Brunauer-Emmett-Teller (BET) method, scanning transmission electron microscopy (STEM), X-ray Absorption Spectroscopy (XAS), and Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy.

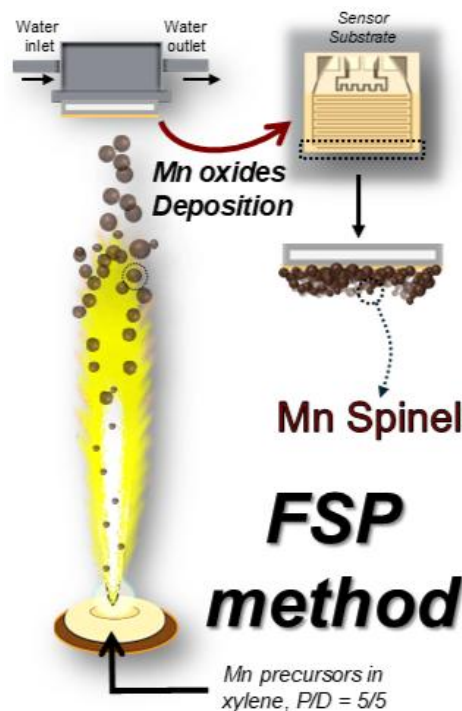


Fig. 1. Schematic illustration of nanoparticles and sensing films of manganese spinel synthesized by the FSP method.

Both sensor materials were tested for the detection of acetone and eleven other interfering gases, including isoprene, ethanol, and methanol, which are relevant interfering analytes in breath analysis. Both materials exhibit high sensitivity for detecting acetone at ppb levels, suggesting an affinity between ketone molecules and manganese-based materials. However, the most notable property of these manganese oxides is their enhanced sensitivity to acetone under humid conditions, as shown in Fig. 2. Both sensors exhibit higher sensitivity to acetone in humid environments than in dry conditions. MnO_x shows the highest normalized response for the detection of 62.5 ppb acetone at 70–80% RH (Fig. 2a), while ZnMn_2O_4 exhibits the highest normalized response at 30–60% RH (Fig. 2b). Considering the absolute (non-normalized) sensitivity to acetone, ZnMn_2O_4 shows a boost of more than 60% under humid conditions (50% RH) compared to dry conditions, whereas MnO_x exhibits a boost of approximately 17% under humid conditions.

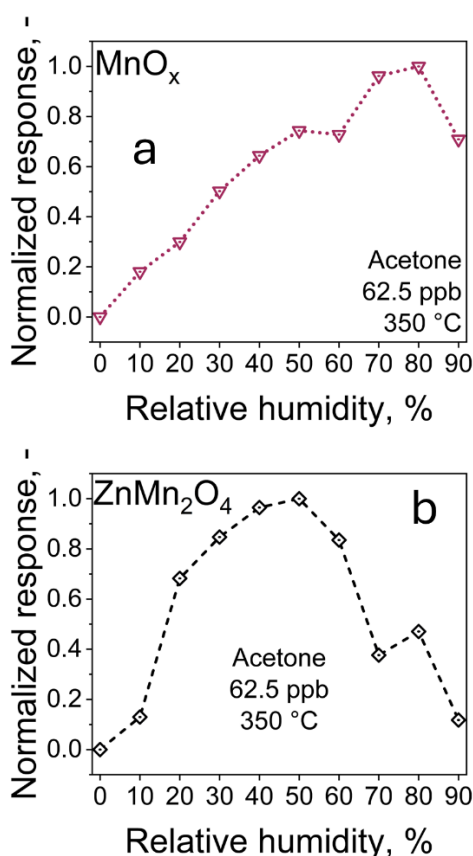


Fig. 2. Normalized sensor response of (a) MnO_x and (b) ZnMn_2O_4 spinels at different RH levels (0–90%) toward 62.5 ppb acetone.

DRIFT spectroscopy was used to investigate the adsorption profiles of MnO_x and ZnMn_2O_4 upon exposure to acetone under dry and humid conditions. Both materials exhibit similar stretching peak profiles; however, the ZnMn_2O_4 surface shows greater perturbation, with sharper and more well-defined bands under humid conditions. Notably, two peaks appear in the 1500 – 900 cm^{-1} region, which are indicative of alkoxy (enolate) intermediates formed during acetone adsorption. Reflecting the presence of $\text{Zn}(\text{T}_d)$ and $\text{Mn}(\text{O}_h)$ sites, these two bands likely correspond to alkoxy species interacting with different surface sites, such as $\text{Zn}-\text{OR}$ and $\text{Mn}-\text{OR}$. This behavior is not observed in MnO_x , which exhibits only a single, broader, less-defined band.

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