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Comparative analysis of WO_3 nanostructures for chemoresistive ammonia sensing

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Summary:

The study compares three metal oxide semiconductor (MOS) sensors based on diverse WO_3 nanostructures for ammonia detection: nanoparticles, nanoflakes, and WO_3-x nanoflowers. Among them, WO_3-x nanoflowers exhibited the highest response and low-power operation (300°C). The results highlight the crucial role of nanostructure morphology and lead to further optimization to enhance response in humid environments for selective ammonia sensor.

Keywords: MOS sensors, chemoresistive sensor, ammonia detection, WO_3 nanostructures, gas sensing

Background, Motivation, and Objective

Despite being a common industrial gas, ammonia (NH_3) is extremely hazardous to human health and the environment because of its high reactivity and toxicity. Even at low concentrations (≥50 ppm), NH_3 can cause irritation to the skin, eyes, and respiratory system [1]. Furthermore, it contributes to air pollution by producing fine particulate matter (PM 2.5), which leads to respiratory and cardiovascular problems [2]. Therefore, the development of highly sensitive and selective NH_3 sensors is essential for use in environmental monitoring, healthcare, and industrial safety applications.

The extensive research into gas sensing applications selects metal-oxide semiconductors (MOS), especially tungsten trioxide (WO_3), because of their high sensitivity and stability, together with their user-friendly manufacturing process. After Shaver first discovered a WO_3-based gas sensor for hydrogen detection [3], a lot of research was done to determine whether WO_3 might be used to detect additional gases such NO_2, NH_3, CO, CH_4, and H_2S. The gas-sensing ability of WO_3 is heavily influenced by its morphology, crystal structure, and synthesis process, which affect critical characteristics as surface area, porosity, and oxygen vacancies [4]. Modifying WO_3 nanostructures enhances NH_3 sensing capability by optimizing response, operating temperature, and humidity interference. However, conventional WO_3-based sensors often operate at high temperatures, resulting in high power consumption and limiting their integration into portable or wearable devices. Despite extensive research on WO_3-based NH_3 sensors, a direct comparison of different WO_3 nanostructures synthesized via various techniques remains limited.

This study compares three WO_3 nanostructures through morphology analysis to enhance NH_3 sensing performance, aiming to develop next generation ammonia sensor with enhanced sensitivity, reduced operating temperature and improved stability under humid conditions.

Materials and methods

WO_3-nanoparticles (WO_3 NPs) were synthesized using sol-gel method. WO_3 nanoflakes (NFs) [5], and reduced tungsten oxide (WO_{3-x} NFLs) nanoflowers were achieved via solvothermal approach followed by washing and drying. The resulting powder was then calcined and characterized by morphological, structural and electrical point of view. The powders were combined with α-terpineol, and ethyl cellulose to form a homogeneous sensing paste. The final paste was screen-printed onto alumina substrates with gold interdigitated electrodes on the front side and a platinum heater on the rear side. The films were sintered at 450°C for 2 hours to increase adhesion, structural stability, and electrical performance.

Results

The scanning electron microscopy (SEM) analysis of three WO_3-based materials demonstrated unique morphological features as shown in Fig. 1. The WO_3 NPs existed as spherical structures, whereas WO_3 NFs displayed a flake morphology. The nanoflower morphology of WO_{3-x} NFLs presented itself as a unique flower-like shape. X-ray diffraction (XRD) analysis of WO_{3-x} NFLs confirms the monoclinic $W_{18}O_{49}$ phase formation.

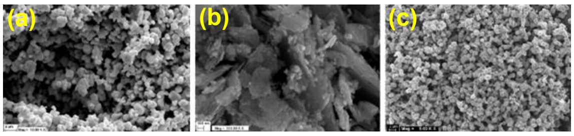

Fig. 1. SEM images of (a) WO_3 NPs, (b) WO_3 NFs, (c) WO_{3-x} NFLs.

The optimal operating temperature was determined by exposing the sensors to 25 ppm of ammonia at various temperatures. The sensitivity measurements were performed at 300 °C while detecting 5, 10, 20, and 50 ppm ammonia concentrations. The dynamic response of NH_3 at varying concentrations is depicted in Fig. 2a, where $W_{18}O_{49}$ nanoflowers outperform WO_3 NPs and NFs in terms of sensing performance and response. This highlights the enhanced performance of the $W_{18}O_{49}$ NFLs across all concentrations.

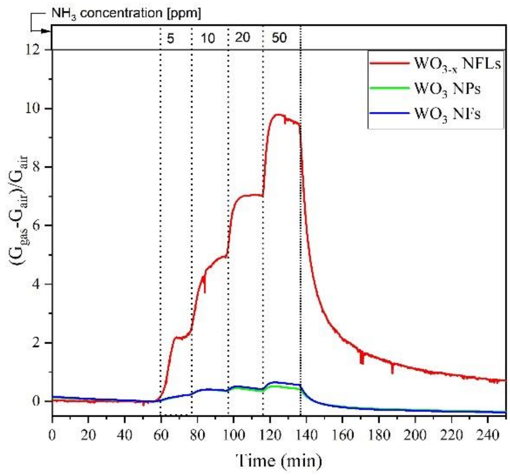

Fig. 2a. Dynamic responses at NH_3 concentration varying from 5-50 ppm.

As seen in Fig. 2b, the sensing performance were also evaluated at 30% of relative humidity (RH%). Sensitivity calibration curves for each of the three samples were displayed under both dry and humid conditions. As expected, humidity reduced responses of all samples, but $W_{18}O_{49}$ NFLs retained the better response, surpassing both WO_3 NPs and NFs. Humidity, however, negatively impacted each sample's response.

About the selectivity, 25 ppm of CO and 100 ppm of H_2 were tested. $W_{18}O_{49}$ NFLs-based sensor exhibited a ten-times higher response to NH_3 than these interferents.

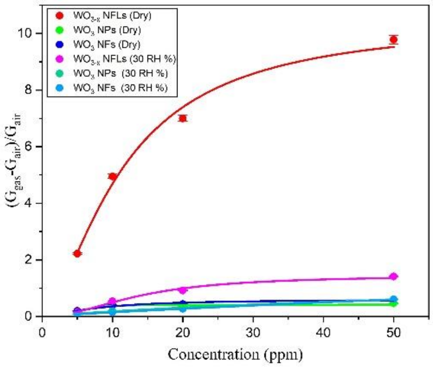

Fig. 2b. Response calibration in dry air and 30 RH%.

Conclusion

The study presents a highly sensitive $W_{18}O_{49}$ NFLs-based sensor for ammonia detection, achieving a remarkable response of at a quite low operating temperature of 300°C. Their improved responsiveness could be attributed to their distinct morphology and oxygen vacancies, showing promise for ammonia sensing applications. However, proper functionalization with Pt and Pd are ongoing to improve performance in humid environments.

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