

Morphology-Governed Diffusion Enables CH₄/H₂ Discrimination in Metal Oxide Chemiresistor

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Summary:

This work reports a single metal oxide-based chemiresistive sensor with microspherical morphology, capable of diffusion-controlled kinetic discrimination between methane and hydrogen under optimized conditions. Briefly, upon exposure to methane gas, we observe a kink in the response curve at the time of introduction. However, upon hydrogen exposure, no such kinks were observed, confirming that the difference in sensing mechanism is visually distinguishable and can serve as an excellent feature for machine learning algorithms to discriminate methane in a hydrogen mixture. These initial results from our investigation indicate the possibility of extending this work to eventually discriminate and classify flammable gases in mixed, real industrial environments without relying on complex material systems with poor stability, reproducibility, and repeatability.

Keywords: chemiresistive gas sensor, In₂O₃ microspheres, methane sensing, porous metal oxide, kinetic discrimination

Background, Motivation, and Objective

Natural gas typically consists of 70% to 95% methane (CH₄) in pipelines, and leakage and the utilization as fuel from these pipelines account for around 30% of the world's carbon emissions [1]. So, there are two effective ways to reduce the carbon emission, first to prevent the leakage from the pipelines while developing a sensor which continuously measures the levels of methane to monitor the status of pipelines around the joints and second by shifting to renewable source of energy by blending hydrogen gas in the existing natural gas pipeline, often known as Hydrogen Enriched Natural gas (HENG) which also tackle the transport issues of highly reactive and flammable hydrogen gas. However, it also brings major safety concerns and sensor challenges of methane leakage detection in the complex blending environment. So, in the first case, a highly sensitive methane sensor can work, and there is plenty of literature showing that researchers have developed metal-oxide chemiresistive sensors through doping, morphology tuning, and heterostructures [2]. But in the second case of blending, the detection of methane in the presence of hydrogen is quite challenging and, to the best of our knowledge, rarely addressed in literature. Generally, methane gas is large, has slow diffusion, and is inert compared to small, reactive hydrogen gas, making the detection of methane over hydrogen quite challenging. In the methane–hydrogen blending environment, we

need a chemiresistive sensor with high methane sensitivity and good selectivity. Thus, to address the above issues, we have fabricated sensors based on In₂O₃ nanomaterials and tested them for CH₄ and H₂ at different temperatures to examine the effect of morphological changes in the sensing material and the kinetic behavior of the gases on the sensing performance.

Description of the New Method or System

The typical synthesis of In₂O₃ involves a two-step process, modified from the literature method to optimize conditions for the desired nanoparticles and microspheres. In the first step, a simple solvothermal method was used to synthesize the In-gly precursor, and in the second step, the sample was heated to high temperature to decompose and form the final In₂O₃ powders. For sensor preparation, 4 mg of sensing material was mixed with 50 µL of 1,3-propanediol solvent and sonicated for 15 minutes to form a uniform dispersion. Then, the sensors were fabricated by drop-casting a 10 µL volume of dispersion onto commercial platinum IDEs on alumina substrates with a 300 µm gap, backside-lining the substrates with a platinum heater. Finally, to decompose and remove 1,3-propanediol from the sensing film, the sensor is heated to 200 °C for 2 hours. A homemade gas-sensing setup with a 35 mL sensing chamber was used for the measurements. Dry air and a gas flow of 100 SCCM were maintained using Bronkhorst mass-flow

controllers, with Methane (0.1%) and Hydrogen (0.1%) from calibrated gas cylinders, which are diluted further with dry air for the desired testing concentration. The electrical resistance of the sensors was measured using Keysight BenchVue. The heater temperature was controlled using an external voltage regulator.

Results

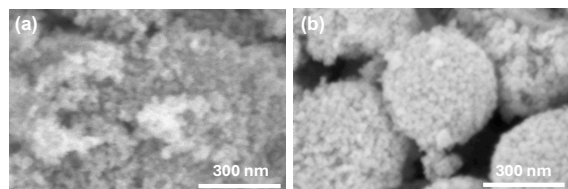


Fig. 1. FESEM images of In_2O_3 nanomaterials (a) nanoparticles (b) microspheres.

Fig. 1 shows the FESEM secondary electron images of synthesized In_2O_3 nanomaterials. FESEM images reveal two distinct morphologies in the synthesized nanomaterials. Fig 1a shows that the In_2O_3 nanoparticles form agglomerated particles. In contrast, Fig. 1b shows that the nanoparticles assemble into a hierarchical pattern to form a well-defined porous spherical shape with a size regime of 300-500 nm.

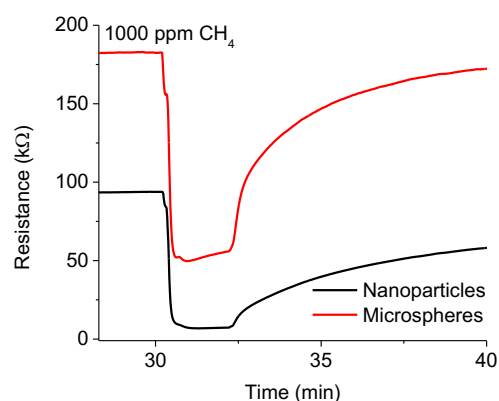


Fig. 2. Methane Sensing performance of In_2O_3 nanoparticles- and microsphere-based chemiresistive sensors at 250 °C and $\leq 5\%$ RH.

Fig. 2 shows the comparative methane sensing performance of two sensors: sensor 1, based on agglomerated nanoparticles, exhibits a larger resistance change than sensor 2, based on microspheres. However, upon closer inspection of the dynamic response kinetics, the nanoparticles exhibit a characteristic steep slope and reach saturation during 4 min of continuous methane exposure. In contrast, in microspheres, on exposure to methane, a kink is observed, and no saturation occurs even after continuous exposure to the gas. This behavior, uniquely observed in the microsphere, indicates the interplay between surface and diffusion reactions; however, the agglomerated particles do not exhibit it. This gave us a good starting point and motivation

to explore the material further, including discrimination between methane and hydrogen.

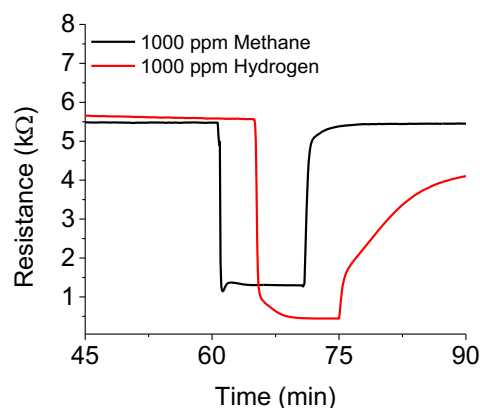


Fig. 3. Sensing performance of In_2O_3 microspheres based chemiresistive sensors at 400 °C and $\leq 5\%$ RH towards 1000 ppm methane gas and hydrogen gas.

As shown in Fig. 3, we tested sensor-2 with a microsphere morphology at 400 °C for hydrogen and methane concentrations of 1000 ppm. As expected, the sensor showed a higher response to hydrogen than to methane. Still, interestingly, the microsphere morphology could discriminate between the hydrogen and methane based on their molecular size and thus controlling the kinetics of the reaction, which eventually gives rise to a distinctive kink in the case of methane sensing, which is due to the slow diffusion of methane due to the bigger size of methane molecules in comparison to hydrogen.

Our work reveals an interesting aspect of morphological change in the diffusion-controlled discrimination between low-reactive and high-reactive flammable gases. Further data will be presented at the conference, including the effect of humidity on sensing performance, optimization of temperature-based discrimination between pure-surface and diffusion-controlled reactions, and an understanding of the methane-sensing mechanism using operando NAP-XPS, which is underway to improve material design and machine-learning algorithms, eventually leading to an industry-ready chemiresistive methane sensor.

References

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