

Sub-ppm Methane Sensing by Spark-Ablation-Synthesized Nano-SnO₂

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We present a scalable spark ablation method for producing Sn nanoparticles at atmospheric pressure, followed by air annealing to form SnO₂. Structural characterization confirms nanocrystalline particles, while XPS reveals a high fraction of adsorbed oxygen species. The resulting sensor detects methane down to 0.2 ppm with strong, repeatable responses and high humidity stability. This performance is attributed to the high surface area and enhanced surface reactivity identified by XPS. Overall, our results demonstrate that spark ablation provides a promising route for reliable low-level methane sensors.

Keywords: Spark Ablation, Methane Detection, MOx Gas sensors, SnO₂ NPs

Metal oxide gas sensors are widely employed in various applications due to their low cost, compactness, and robustness. However, their sensitivity and selectivity at low analyte concentrations remain insufficient for environmental monitoring, motivating the development of improved nanostructured sensing materials. [1]

While conventional synthesis approaches such as sol-gel and hydrothermal methods dominate [2], dry techniques like flame spray pyrolysis and spark ablation offer distinct benefits, including reduced contamination, continuous production, and direct formation of porous structures. [3] Spark ablation, in particular, is an environmentally friendly method that produces high-purity nanoparticles through repetitive electrical discharges between conductive electrodes, followed by rapid cooling and particle formation. The technique, was initially introduced by Schwyn et al. [4] and to date, it has been successfully employed for the synthesis of catalytic, sensing and photovoltaic nanomaterials among others [5].

In this work, [6] Sn nanoparticles are generated using atmospheric-pressure spark ablation with N₂ as a carrier gas and subsequently collected and annealed. The resulting SnO₂ nanoparticles form agglomerates with an average mobility diameter of ~80 nm, while BET analysis indicates a decrease in specific surface area from 105.5 m²/g (as-prepared Sn) to 45 m²/g after annealing due to sintering effects. The sensing film, fabricated via doctor blading, exhibits a highly porous

and interconnected morphology (see Figure 1), as observed by scanning electron microscopy (SEM), facilitating efficient gas diffusion and surface interaction. [7]

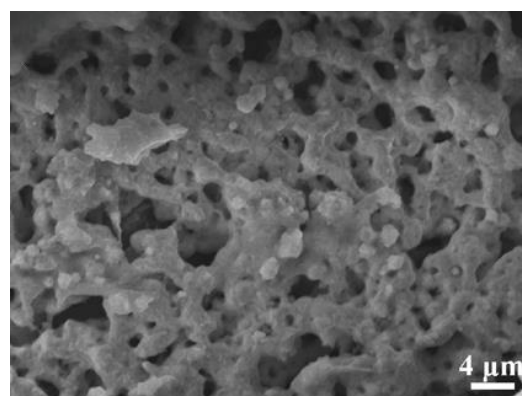


Figure 1. SEM image of the porous sensing film composed of annealed SnO₂ nanoparticles.

The fabricated sensing film, operated at 275 °C for methane detection, reliably measured concentrations between 0.2 and 10 ppm at 20% relative humidity (see Figure 2) with a signal-to-noise ratio of ~58 and a theoretical detection limit of ~7 ppb. Additionally, it exhibited high repeatability over more than ten consecutive cycles at a fixed concentration of 5 ppm (see Figure 3). Furthermore, when exposed to 10 ppm methane, the sensor response remained stable across a broad humidity range (20–80% RH), with variations below 10%. This demonstrates robust performance under varying environmental conditions, highlighting the suitability of the sensor for real-world applications.

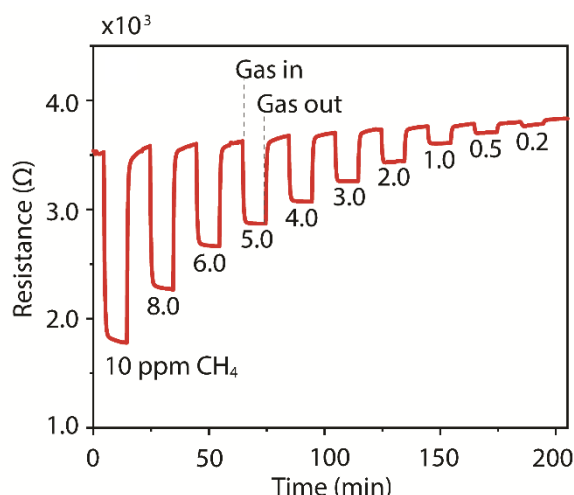


Figure 2. Sensor resistance changes during repeated exposure to different methane concentrations over time at 275 °C and 20% RH.

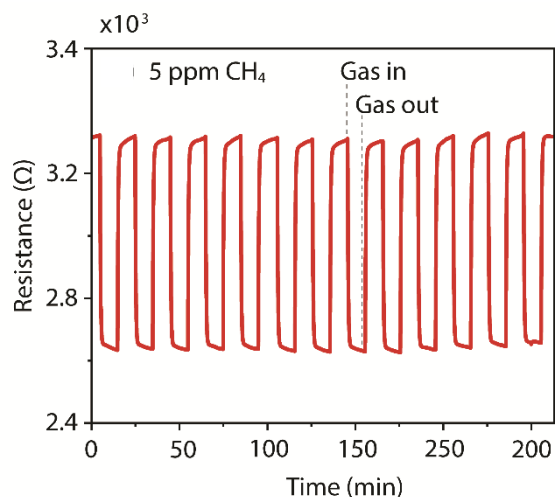


Figure 3. Sensor resistance as a function of time at a constant methane concentration of 5 ppm over 13 cycles at 275 °C and 20% RH.

The performance of the sensor was evaluated in the presence of interfering gases including acetone, ethanol, hydrogen, carbon monoxide and ammonia and was found to follow the behavior of other SnO₂ sensors reported in the literature.

The enhanced sensing performance is linked to the structural and surface characteristics of the nanoparticles, particularly the increased proportion of adsorbed oxygen species revealed by XPS, which facilitates charge transfer during methane oxidation. Overall, this study demonstrates that spark ablation is a powerful and versatile technique for producing high-performance sensing materials, offering a promising route toward reliable sub-ppm methane detection for environmental and industrial applications.

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