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Sub-ppm Methane Sensing by Spark-Ablation-Synthesized SnO_2 Nanoparticle-based Materials

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We demonstrate a simple and scalable method to synthesize Sn nanoparticles via spark ablation using nitrogen at atmospheric pressure. Post-annealing, the particles convert to SnO_2, as confirmed by X-ray diffraction and Transmission Electron Microscopy (TEM), and processed into gas sensing materials for methane detection. The sensors respond to concentrations as low as 0.2 ppm with high sensitivity and repeatability. Performance remained stable over repeated cycles. Our results demonstrate that spark ablation provides a promising route for fabricating reliable low-level methane sensors.

Keywords: Spark Ablation, Methane Detection, MOx Gas sensor, SnO_2 NPs

Metal oxide gas sensors play a crucial role in a number of applications. Despite their advantages such as high sensitivity, stability, low cost, small size and low power consumption, however, we currently lack sensors that are sensitive and selective enough for applications in environmental monitoring[1], underlining an important need for further efforts to improve their performance.

Metal oxide nanoparticles are predominantly synthesized using wet chemical methods for instance sol-gel or hydrothermal techniques[2]. However, emerging dry methods, including flame spray pyrolysis and spark ablation offer distinct advantages, such as improved contamination control, single-step synthesis and the ability to directly deposit porous films[3]. Spark ablation, which is an environmentally friendly technique that produces high-purity nanoparticles with controlled size and composition, provides also a very good alternative. The technique, initially introduced by Schwyn et al.[4], produces nanoparticles via repeated spark discharges between two conductive electrodes, evaporating small amounts of material from their heated surface, and forming nanoparticles upon quenching. To date, it has been successfully employed for the synthesis of catalytic, sensing and photovoltaic nanomaterials among others[5].

Here we employ atmospheric-pressure spark ablation, using N_2 as a carrier/quenching gas and two Sn electrodes (2 mm in diameter), to produce Sn nanoparticles. The particles produced are agglomerates, with an average mobility diameter of approximately 80 nm and a geometric standard deviation (GSD) of 1.57. BET measurements of the collected nanoparticle powders have a specific surface area of 105.5 m^2/g for the as-prepared Sn nanoparticles, which decreases to 45 m^2/g after thermal annealing. Upon annealing the pure Sn nanoparticles also convert to SnO_2. The crystallite size of the SnO_2 in the annealed samples was determined to be 15 nm. The sensing film, fabricated via doctor blading, was further characterized using scanning electron microscopy (SEM), which revealed a highly porous and uniform network with pore sizes ranging from the nanometer to micrometer scale (cf. Figure 1). This porous structure is expected to enhance gas diffusion, making it well-suited for sensing applications[6].

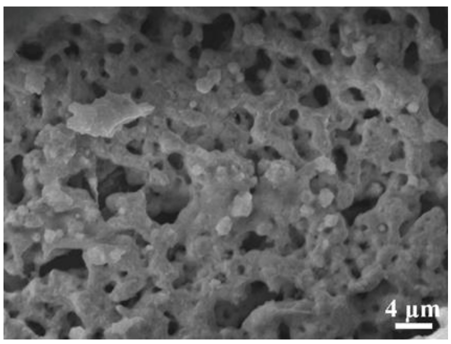

Figure 1. SEM image of the porous sensing film comprised by annealed SnO_2 nanoparticles.

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The resulting sensors, designed for methane detection and operating at 275 °C, successfully detected concentrations ranging from 0.2 ppm to 10 ppm at 20% relative humidity (cf. Figures 2 & 3). In addition, they demonstrated excellent response and repeatability over more than 10 cycles at a constant methane concentration of 5 ppm.

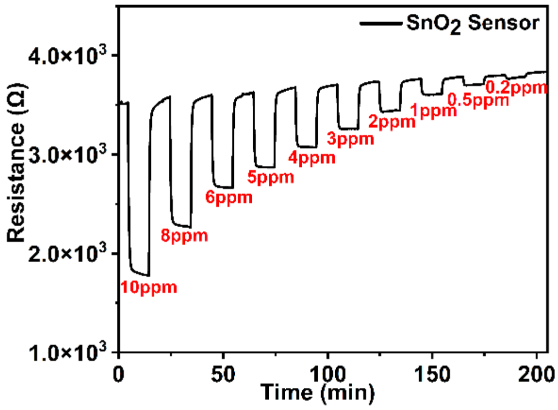

Figure 2. Resistance of the sensor as a function of time, while the concentration of methane in the overlaying gas ranged from 0.5 to 10ppm.

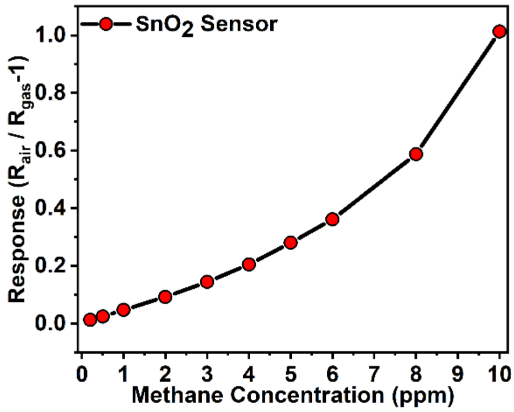

Figure 3. Response of the sensor as a function of methane concentration.

The performance of the sensor was evaluated in the presence of water vapor and interfering gases including acetone, ethanol, hydrogen, carbon monoxide and ammonia. Its response to a constant methane concentration of 10 ppm remained stable across relative humidity (RH) levels ranging from 20 to 80%. Variations in response were consistently below 10%, indicating that the sensor operates reliably under different humidity conditions, ensuring its suitability for diverse environmental applications.

Our results show the potential of spark ablation for synthesizing high-performance methane sensors, addressing the critical need for reliable sub-10 ppm detection. The approach is simple, scalable and well-suited for real-world environmental and industrial monitoring applications.

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