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

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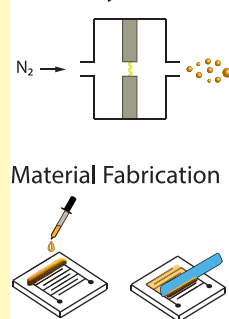


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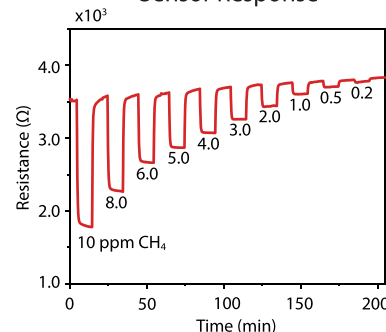
ABSTRACT: Methane is considered one of the cleanest energy sources as it produces fewer pollutants upon burning compared to other fossil fuels. Its accidental release during extraction, transportation, and use, however, poses significant environmental and safety risks, warranting advanced sensing technologies to monitor its concentration in ambient air. Here, we prepare nanoparticle-based materials for sensing methane at concentrations that are highly relevant in the atmospheric environment. The nanoparticle (NP) building blocks of the sensing materials are produced by spark-ablating and simultaneously quenching Sn electrodes with a N₂ flow at atmospheric pressure. The resulting Sn NPs are subsequently collected and oxidized to SnO₂ by thermal annealing in ambient air before doctor blading them onto substrates with interdigitated electrodes. The synthesized materials were characterized by X-ray diffraction and photoelectron spectroscopy, Brunauer-Emmett-Teller analysis, as well as atomic force, transmission, and scanning electron microscopy. The results show that our sensing materials can quantify methane concentrations down to 0.2 ppm, having a signal-to-noise ratio of 58 and a theoretical limit of detection of ca. 7 ppb. What is more, they maintain excellent robustness across a relative humidity range of 20–80% and exhibit a high cycling stability and repeatability; features that render them superior compared to other metal oxide semiconducting materials reported in the literature so far. Based on our measurements, we also offer new insight into how the NP synthesis process can affect sensor sensitivity, demonstrating a correlation between spark-ablation energy and NP size, which in turn determines the crystal size, the specific surface area, as well as the fraction of adsorbed oxygen on the surface of the sensing material, and consequently its interaction with the target gas. Combined with the simplicity of their preparation, these sensing materials hold great potential for a wide range of environmental and industrial applications.

KEYWORDS: metal oxide gas sensors, aerosol-based synthesis, nanoparticles, nanomaterials, thin films

Particle Synthesis



Sensor Response



Methane, the primary component of natural gas, is considered one of the cleanest fossil fuels due to its higher calorific value and low emissions of pollutants, rendering it widely used for power generation, heating and transportation.¹ At the same time, however, methane has a high global warming potential that is 30 times more than that of carbon dioxide over a 100-year span, making it the second most impactful anthropogenic greenhouse gas.² Considering the growing use of natural gas, which has increased atmospheric methane emissions by almost 170% since pre-industrial times,³ its potential emissions are of great concern as they provide a strong accelerator of global warming and a major contributor to climate change.⁴

Unwanted release of natural gas during its production, transportation and use accounts for up to 25% of total methane emissions,⁴ which apart from the environmental hazards described above, they represent significant economic losses.⁵ At the same time, the flammability of methane poses serious safety risks, as it forms explosive mixtures at concentrations between ca. 5% and 15% in the atmosphere.⁶ This creates a pressing need for reliable

monitoring of methane concentrations in the atmospheric environment through distributed sensor networks that can be installed and used easily across various production and transportation lines.

Methane in ambient air can be detected and measured by optical,⁷ calorimetric,⁸ pyroelectric,⁹ electrochemical,¹⁰ as well as chemiresistive methods that employ semiconducting metal oxide materials.¹¹ The latter have been extensively investigated due to their low cost, ease of manufacturing and portability, as well as their high sensitivity and robustness.¹² Among all metal oxides, SnO₂, which is an n-type semiconductor, offers a great solution because it exhibits a band gap of 3.6 eV that attributes a low

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intrinsic conductivity, excellent thermal and chemical stability when exposed to ambient air, as well as high surface reactivity.¹³ In fact, the high reactivity of SnO₂, modulated by the presence of oxygen vacancies and other reactive species that can ionosorb on its surface, makes it highly chemoresponsive. As a result, it has been widely used for detecting typical reducing gases, including methane, towards which it exhibits a notable sensitivity.¹¹

One limiting factor of using metal oxide films, including SnO₂, for measuring the concentration of gases in ambient air such as methane, is their low selectivity.¹⁴ This, however, can in large be overcome by adding catalytic layers on top of the films that act as active filters.¹⁵ Examples for such catalytic layers are Pt on Al₂O₃, Pt on TiO₂, Pt on CeO₂, or Pt on ZrO₂, that effectively eliminate volatile organic compounds, CO and other common interfering gases. This can increase methane selectivity, qualifying these sensors applicable to real-world conditions.¹⁶ Considering that, the next challenge in advancing metal oxide sensors for atmospheric applications is the development of highly porous structures and well-defined crystals or nanoparticles (NPs),¹⁷ which are essential for enhancing gas adsorption and improving overall sensor performance.

While a number of research groups have explored the capabilities of SnO₂-based methane sensors, the reported detection sensitivity (or limit of detection; LOD) typically range from a few tens of parts per million (ppm) to a few percent. This is adequate for using these materials to build detectors that can identify if methane in certain environments exceeds the flammability level and thus ensure its safe use.¹⁸ To monitor the concentration of methane in ambient air, however, the LOD of the sensors needs to be as low as 2 ppm, which is the background concentration of methane in the atmospheric environment.¹⁹ This warrants new methods for producing sensing materials that exhibit improved LOD, resolution, higher signal-to-noise ratio (SNR), and faster response compared to most of the current state-of-the-art solutions, yet at affordable cost. Such sensors are essential for distributed monitoring of methane concentrations in the atmospheric environment, enabling identification of unwanted emission sources to mitigate their associated impacts.

Here we report a new preparation method of sensing nanostructured materials capable of detecting and measuring the concentration of methane down to sub-ppm levels. The building blocks of the sensing materials are Sn-based NPs synthesized by spark ablation, which is a continuous and environmentally friendly method.²⁰ To produce the sensing films, the synthesized NPs, collected in the form of a powder, were subsequently annealed and doctor-bladed onto interdigitated electrodes. Although spark ablation, followed by other depositions techniques such as direct impaction or electro-deposition, has been employed to produce NP building blocks for sensing elements targeting a wide range of gases, including NH₃,²¹ NO₂,²² CO,²¹ H₂S,²¹ H₂,^{23,24} the detection of low concentrations of methane has not been demonstrated, despite the immediate relevance for environmental monitoring. Under this consideration we also benchmarked its response, its stability and its recovery times over atmospherically relevant humidity ranges.

■ EXPERIMENTAL

NP Synthesis and Characterization

Sn NPs were synthesized by a spark discharge generator (SDG; VSP-G1) with two tin rod electrodes (2 mm in diameter, 99.75% purity; Goodfellow) and high purity N₂ flow (99.999%; 3 L/min) as a carrier

gas as illustrated in Figure 1a. The current and voltage on the SDG were kept constant at 3.0 mA and 1.00 kV, respectively. With the capacitance fixed at 20 nF, the input energy was 22.5 mJ, at a frequency of 100 Hz, and the calculated production rate 1.1 mg/h.²⁵ The Sn NPs from the resulting aerosol downstream of the SDG were deposited on water-wettable PTFE filters (0.45 μm, Pall Corporation). The NP-containing powder collected on the filters was subsequently thermally annealed under ambient air in a kiln, where the temperature was gradually increased from ambient to 500 °C at a heating rate of 3 °C/min, and maintained at that temperature for 5 hours, facilitating the formation of SnO₂. Both the Sn (in the as-prepared sample) and SnO₂ (in the sample after annealing) NPs were characterized using the techniques described below.

The size distributions of the NPs produced by the SDG were determined using a scanning mobility particle sizer (SMPS), comprised of a Differential Mobility Analyzer (DMA, TSI model 3786) for particle classification and a Condensation Particle Counter (CPC, TSI model 3085) for particle counting. Due to the high particle concentration (>10⁸ particles/cm³) produced directly by the SDG, a simple dilution system with HEPA filters was employed to reduce the particle concentration to levels suitable for accurate measurement by the SMPS, as described elsewhere.²⁶

The crystal structure of the NPs before and after annealing was determined by X-ray Diffraction (XRD; Rigaku Miniflex 600), employing monochromatized Cu-Kα radiation (λ = 1.5406 Å). The measurements were conducted over a 2θ range of 20° to 80° and a scanning speed of 0.01°/s. The crystallite size was calculated using the Scherrer equation expressed as:²⁷

$$D = \frac{k \times \lambda}{\beta \times \cos \theta} \quad (1)$$

where β = 0.5725 is the full-width half maximum of the peaks in the XRD spectra, θ = 16.867° is the Bragg angle, k = 0.94 is the Scherrer constant, and λ = 1.5406 Å the wavelength of the X-ray.

The specific surface area (SSA) of the NPs, immediately after synthesis and after annealing, was determined by the Brunauer-Emmett-Teller (BET) method using multi-point nitrogen adsorption at 77 K. The amount of nitrogen adsorbed was measured at various relative pressures (P/P₀) using a gas adsorption analyzer (Sync 100 Series, 3P Instruments). Prior to the measurements, the samples were degassed under high vacuum conditions. The sample of the as-deposited NP powder was degassed at 30 °C to avoid oxidation for 24 hours, while the sample with the powder after thermal annealing was degassed at 200 °C for 3 hours. The BET particle diameter of the powder was calculated by:

$$d_{\text{BET}} = \frac{6}{\text{SSA}_{\text{BET}} \times \rho_m} \quad (2)$$

where SSA_{BET} is the specific surface area (m²/g) and ρ_m is the density of Sn and SnO₂ (g/cm³).

The morphology of the NPs and the sensing material was characterized by Transmission Electron Microscopy (TEM; Jeol JEM-3000F), Scanning Electron Microscopy (SEM; Zeiss EVO 15) and Atomic Force Microscopy (AFM; Park NX10). For the annealed NPs, the TEM sample was prepared by drop-casting a small amount of an ethanol-based solution containing the NPs onto a TEM grid. The SEM analysis was conducted on the final sensing element (film), placed horizontally to examine its morphology or vertically to determine its thickness.

To gain insights into the surface chemical mechanisms that define the sensing behavior of the resulting materials we also carried out X-ray photoelectron spectroscopy (XPS). These measurements were conducted using Al Kα radiation (microfocussed, 10–400 μm) under ultra-high vacuum (5 × 10^{−9} mbar or better; Nexsa G2, Thermo Scientific, USA). Peak fitting was performed using the Advantage

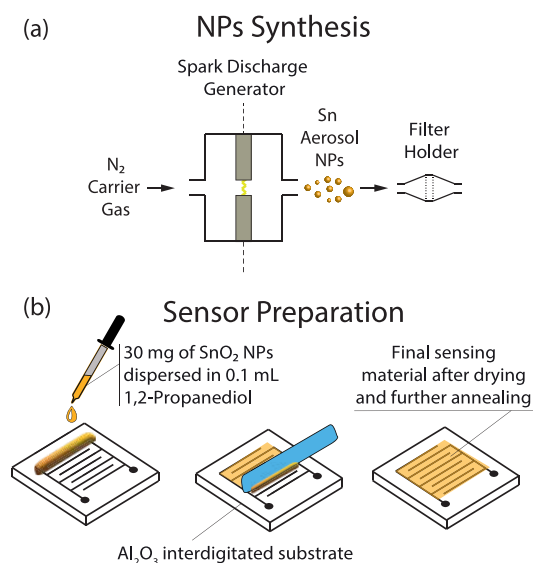


Figure 1. Schematic of the experimental setup and the process followed to prepare the sensing materials. (a) Synthesis step: NPs generated by a spark discharge generator were collected on filters using a filter holder. (b) Preparation step: the collected and annealed NPs were deposited using the doctor blading technique.

software package (Thermo Scientific, USA), whereas all the binding energies were estimated based on a calibration with the C 1s signal of adventitious carbon at 284.8 eV.

Sensor Fabrication and Testing Setup

The process to produce the sensing materials (in the form of films) is illustrated in Figure 1b. More specifically, 30 mg of SnO₂ NPs (i.e., the annealed powder) were dispersed in 0.1 mL 1,2-Propanediol (Sigma-Aldrich, ≥99.5%). The mixture was ground in a mortar to form a uniform paste, which was then deposited onto a commercial alumina substrate with interdigitated platinum stripes on one side and a platinum heater on the other (Electronics Design Center CWRU, Sensor #103), using the doctor blade coating technique. The resulting sensing elements were left to dry at room temperature for 4 hours and placed in an oven maintained at 80 °C for at least 12 hours. The resulting sensing materials were annealed in an oven at 300 °C for 30 min under ambient air prior to the tests in order to ensure that the sensing films were completely dried and their conductivities stabilized.

The sensing elements were then mounted on a custom-designed Macor holder with spring-loaded pins to power its heating element and measure resistance changes of the film during the tests. The holder was placed inside an airtight 100 cm³ resin testing chamber, having an inlet and an outlet, where the sensors were positioned vertically to the gas flow.

The gas flow over the sensors was regulated using two mass flow controllers (MFCs; Alicat Scientific, MC series), while the total flow rate was maintained constant at 0.3 L/min. During the measurements, synthetic air (99.999% purity, with trace concentrations of C_nH_m and NO_x ≤ 100 ppb and relative humidity (RH) of ca. 20% at 23 °C) was mixed at various ratios with gas from a cylinder containing 14 ppm methane in N₂. With this setup we were able to produce gas mixtures having methane concentrations down to the ppb level. The electrical resistance of the sensing materials was measured by an electrometer (Keysight B2987B, USA) while being heated with an independent power supply (Votcraft VLP2403). At the start of each experiment, the sensors were stabilized at their working temperature for at least three hours while dry synthetic air was continuously passed through the testing chamber. Once stabilized, the sensor exhibited

highly repeatable responses and did not require long re-stabilization periods before subsequent measurements. After stabilization, the sensors were exposed to the target gas at a specified concentration for 10 min, followed by 10-min flushing with synthetic air.

Sensor selectivity was tested on a gas-mixing setup described elsewhere.²⁸ The overall gas flow was kept constant at 0.3 L/min using high precision MFCs (Bronkhorst, Netherlands). In these tests, the RH was fixed at 20% by flowing synthetic air (Linde, Switzerland, 5.0, CnHm and NO_x ≤ 100 ppb) through a deionized water bubbler at 23 °C. The concentration of the gases was controlled by dosing gas standards (all in synthetic air, from Linde, Switzerland) into the humidified air stream: CO (506 ppm), H₂ (47.9 ppm), ethanol (15.0 ppm), acetone (18.1 ppm) and ammonia (15 ppm). Similarly to the rest of the experiments, the electrical resistance of the sensing materials in the selectivity tests was measured with a multimeter (Keithley, Integra Series 2700, USA), while heating was supplied through the back heater of the substrate with a power source (R&S HMC803, Switzerland). Prior to the first analyte exposure, the sensing materials were left for a few hours until a stable baseline was reached. For each measurement, the sensor was exposed until the response of the sensor reached a steady state response. Between the different analyte exposures, the sensor was left in clean humidified (20% RH) air until they fully recovered before being tested again.

SnO₂ is an n-type metal-oxide semiconductor, while methane is a reducing gas. As a result, the sensing response was determined as:

$$\text{Response} = \frac{R_{\text{air}}}{R_{\text{gas}}} - 1 \quad (3)$$

where R_{air} and R_{gas} denote the resistance of the sensing material in synthetic air measured immediately before each gas exposure cycle and in the presence of methane, respectively. The response and recovery times were defined as the time required to achieve 90% of the total resistance change.

The SNR of the sensor was calculated using the formula:

$$\text{SNR} = \frac{\Delta R}{\text{Noise}} \quad (4)$$

where ΔR is the change in resistance upon exposure to a specific methane concentration and Noise is defined as the standard deviation of the baseline resistance measured over at least 1 minute before gas exposure. We should also note here that according to the definition by the International Union of Pure and Applied Chemistry (IUPAC), the theoretical limit of detection is the analyte concentration at which the resistance change of the sensor is three times the noise level of the baseline resistance.²⁹

RESULTS AND DISCUSSION

Materials Characterization

Figure 2a shows the size distributions of the tin NPs measured immediately downstream the SDG with the SMPS. Due to the high particle concentrations produced by the SDG, a 330-fold dilution was applied and the size distributions were corrected accordingly. We should note here that the particles produced by the SDG under typical conditions are agglomerates (i.e., comprised of smaller primary particles),³⁰ having an average mobility diameter of ca. 80 nm and a geometric standard deviation (GSD) of 1.57. Similar sizes and GSDs are reported for other metallic NPs produced by SDG, such as Al.²⁶ In contrast, flame-made SnO₂ particles exhibit larger sizes (typically larger than ca. 120 nm) and significantly broader size distributions (GSD of 3.6).³¹

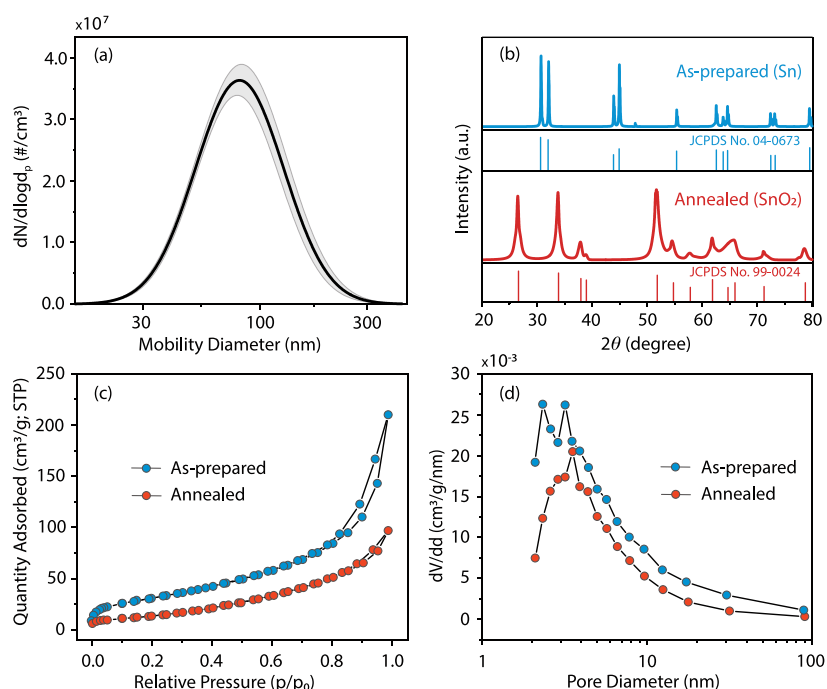


Figure 2. Characterization of the as-prepared and annealed NPs, including: (a) size distributions of NPs produced by the SDG, measured by the SMPS with the thick black line indicating the averaged distribution and the grey shaded area corresponding to the one standard deviation (1.24) range, (b) XRD patterns of the as-prepared (blue line) and annealed (red line) NPs with their corresponding libraries (JCPDS No. 04-0673 for Sn and JCPDS No. 99-0024 for SnO_2), (c) N_2 adsorption-desorption isotherms, and (d) Barrett–Joyner–Halenda pore size distributions.

Figure 2b shows the XRD patterns of our samples. The top diffractogram in this figure is from an as-prepared sample, exhibiting four principal peaks at $2\theta \approx 30.6^\circ$, 32.0° , 43.9° and 44.9° that correspond to the (200), (101), (222) and (211) planes of tetragonal Sn (JCPDS No. 04-0673), respectively. The XRD pattern after annealing in air (bottom diffractogram) indicates a completely oxidized powder, with peaks corresponding to cassiterite SnO_2 . The three main diffraction peaks of tetragonal SnO_2 are observed at $2\theta = 26.4^\circ$, 33.7° and 51.6° , corresponding to the (110), (101) and (210) crystal planes (JCPDS No. 99-0024), respectively. Using eq 1 and the data from the (101) plane, the SnO_2 crystallite size in the annealed samples was determined to be ca. 15.0 nm. This coincides with the physical size of the particles determined by TEM analysis (see Figure 3d and discussion below) that is estimated to be ca. 15.1 nm, indicating that the NPs are monocrystalline.

Figure 2c shows the N_2 adsorption-desorption isotherms, where both the as-prepared and annealed samples exhibit IV-type physisorption isotherm with an H3-type hysteresis loop.³² This indicates multilayer adsorption due to the presence of non-rigid aggregates, and the absence of limiting adsorption at high pressures. The BET measurements show an SSA of $105.5 \text{ m}^2/\text{g}$ for the as-prepared sample (consisting of Sn NPs), decreasing to $45 \text{ m}^2/\text{g}$ after thermal annealing (sample consisting of SnO_2 NPs) due to the thermally induced sintering.³³ Figure 2d provides the Barrett–Joyner–Halenda pore size distributions for both materials. The most frequent and prominent peaks for the as-prepared and annealed samples are 2.33 and 3.54 nm, respectively, indicating for both cases a mesoporous structure that results from how the primary particles, having diameters in the 10–20 nm range, are arranged in the sensing material. This mesoporous structure is important as it increases the

active surface area of the sensing material, thereby enhancing the sensitivity of the sensor.³⁴ The annealing process promotes particle growth through sintering, resulting in a reduction of SSA, surface defects and porosity, in line with the increased pore diameter. The particle diameter of the SnO_2 NPs, estimated by the BET measurements using eq 2, has a value of 19.2 nm, which also agrees with the results obtained by TEM and XRD.

The morphology and structure of the sensing material determined by SEM is provided in Figure 3a. The material exhibits a highly porous and uniform NP network, with pore sizes varying from the nanometer to the micrometer scale, which is ideal for gas sensing applications as it facilitates enhanced interaction with the target gas.³⁵ The average thickness of the sensing material, determined by measurements at 10 different locations of the film on the cross-sectional SEM imaging (see Figure 3b), was ca. $35 \mu\text{m}$. This cross-sectional image also illustrates the internal structure and layer morphology of the particulate-based film adhered to the alumina substrate. AFM analysis also showed a moderately rough and textured surface as illustrated in Figure 3c. The root mean square roughness was estimated to be ca. 100 nm, indicating moderate height variations across the film surface, whereas the surface area ratio was 86%, indicating a substantial increase in actual area relative to a flat plane. These morphological features are advantageous for gas sensing, as the enhanced roughness and expanded surface area provide more active sites accessible for gas adsorption,³⁶ thus facilitating stronger interactions between gas molecules and the sensing layer, potentially leading to improved sensor response. Figure 3d shows a TEM image of agglomerated and fractal-like SnO_2 particles, comprised of polygonal shaped primary particles having sizes that range from 10 to 20 nm, with a mean size

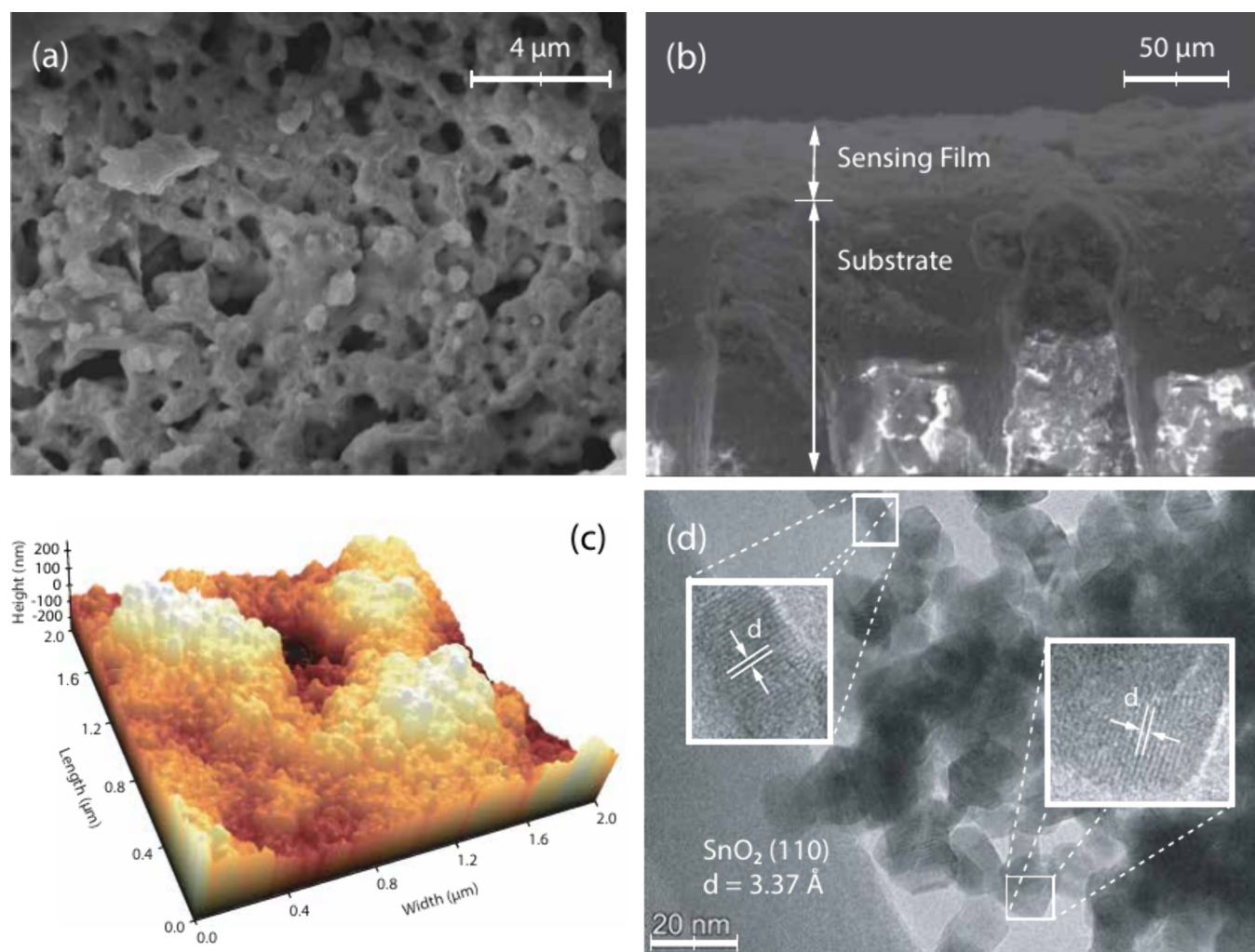


Figure 3. Microscopy analysis including (a) SEM image of the sensing material comprised of the SnO_2 NPs, (b) SEM image of its cross section, having a thickness of ca. $35\ \mu\text{m}$, (c) AFM image of the sensing material over an area of $2 \times 2\ \mu\text{m}^2$, and (d) TEM image of the annealed NPs showing that the lattice distance corresponds to that of the (110) plane of tetragonal SnO_2 .

of 15.1 nm. The spacing between the lattice planes of the primary particles was $3.37\text{\AA}$, corresponding to the d_{110} plane of tetragonal SnO_2 , further confirming the XRD measurement (Figure 2b).

Gas Sensing Performance

As the gas sensing performance of semiconducting gas sensors is strongly influenced by the working temperature, the response of the SnO_2 sensor was investigated over a range of 100 to $330\ ^\circ\text{C}$ (Figure 4a). The sensor response increased with temperature and appeared to level off above $150\ ^\circ\text{C}$ with the highest value being observed at $275\ ^\circ\text{C}$. This temperature is within the typical range of 200 to $400\ ^\circ\text{C}$ reported in the literature for similar SnO_2 sensors for methane,³⁷ and was selected as the temperature for all subsequent tests.

Results from the performance tests of the sensor, including changes in resistance and sensor response for gas concentrations ranging from 0.2 to 10 ppm, are provided in Figure 4b. The sensor responds to all the methane concentrations with a distinguishable resistance reduction, as expected for n-type SnO_2 . After methane exposure, the initial resistance baseline is always recovered, indicating fully reversible analyte-surface

interaction. That way, even the lowest tested concentration of 0.2 ppm is clearly identified with an SNR (eq 4) exceeding 58, while the extrapolated (theoretical) limit of detection, estimated as 3 times the noise level of the sensor baseline resistance, is ca. 7 ppb. With increasing methane concentration, the response increases exponentially from 0.26 at 5 ppm and over 1.01 at 10 ppm (Figure 4c), demonstrating that its resolving power is high enough to quantify incremental changes above the background concentration. The sensor demonstrated response and recovery times of 58 and 79 s, respectively, at 5 ppm (Figure 4b), which is considered sufficient for environmental monitoring.

A crucial requirement for gas sensors in practical applications is stability and repeatability. Those were tested at a constant methane concentration of 5 ppm over 13 consecutive cycles (see Figure 4d, and corresponding Figure S1 in the Supporting Information), demonstrating excellent repeatability, with an average response of 0.26 and a relative standard deviation of ca. 0.2%.

Figure 4e shows the response of the sensor at RH values ranging from 20 to 80%, when exposed at a constant methane concentration of 10 ppm. Evidently, the response of the sensor

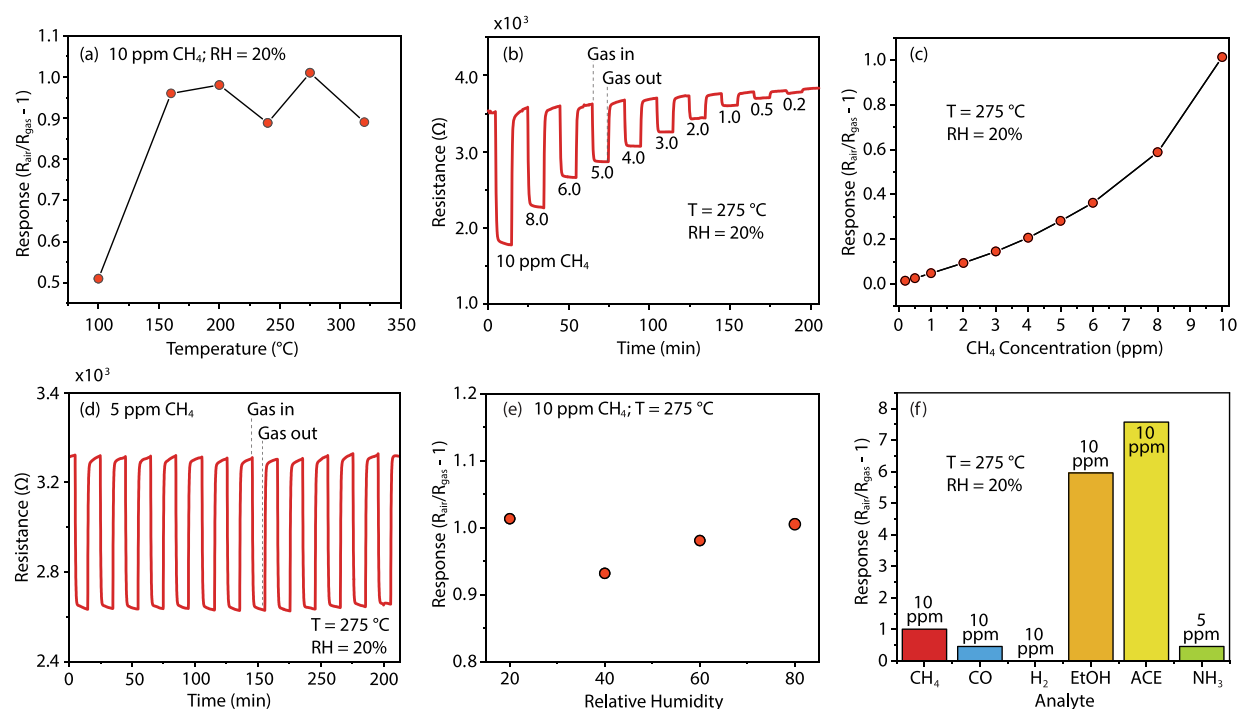


Figure 4. Gas sensing performance of the SnO_2 sensor, including (a) sensor response to 10 ppm methane at temperatures ranging from 100 to 330 °C and 20% RH, (b) sensor resistance changes during repeated exposure to different methane concentrations over time at 275 °C and 20% RH, (c) sensor response as a function of methane concentration ranging from 0.2 to 10 ppm at 275 °C and 20% RH, (d) sensor resistance as a function of time at a constant methane concentration of 5 ppm over 13 cycles at 275 °C and 20% RH, sensor response (e) as a function of RH at a constant methane concentration of 10 ppm at 275 °C, and (f) to various gases, including methane (CH_4), carbon monoxide (CO), hydrogen (H_2), ethanol (EtOH), acetone (ACE), and ammonia (NH_3) at 275 °C and 20% RH.

remained largely unaffected by RH, with variations consistently below 10%, indicating that it maintains reliable performance under varying humidity conditions, thus making it suitable for measurements in ambient air.

The selectivity of the sensing materials was also investigated (see Figure 4f) and found to follow the behavior of other SnO_2 sensors reported in the literature. While it features reasonable methane selectivity over CO and H_2 , it is interfered by ethanol and acetone. As pointed out in the introduction, this can be addressed with catalytic films as active filters¹⁵ (e.g., ZnO ³⁸) that are rather effective in the removal of volatile organic compounds, thereby making these sensors applicable to real-world conditions.¹⁶

Insights into the Sensing Mechanism

The sensing performance of the materials we produce depends on the structural characteristics of the NP building blocks, which in turn can be tuned by the operating parameters of the SDG. Figure 5a compares the response of two materials made with NPs that have been synthesized by the SDG under different conditions. The NPs employed in the primary materials were produced by operating the SDG at 3.0 mA and 1.00 kV, having a crystallite size of 15.0 nm and a specific surface area of 45.0 m^2/g upon annealing as discussed above (see Figure 2). The variant material was prepared with NPs produced by operating the SDG at 6.5 mA and 1.36 kV, yielding a larger crystallite size (22.2 nm) and a lower surface area (33.5 m^2/g) upon annealing (see Figure S2 in Supporting Information). Evidently, the primary material exhibits a consistently higher response, with the

difference from the variant reaching up to 14% when exposed at 10 ppm CH_4 , highlighting the role of the structural properties in determining sensor behavior.³⁹ To the best of our knowledge, such direct comparison in the performance of materials produced with NPs synthesized under different operating conditions has not been reported previously.

To gain insight into the potential differences in the surface chemistry among materials employing NPs that are produced in different ways we carried out XPS analysis (see Figures S5b–d). Evidently, the O1s spectra show that the primary material (produced by operating the SDG at 3.0 mA and 1.00 kV; see Figure 5b) contains a substantially larger fraction of higher binding energy oxygen species (O_{ads}), relative to lattice oxygen (O_{latt}), compared to the variant material (i.e., when operating the SDG at 6.5 mA and 1.36 kV; see Figure 5c), with the resulting $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratios being 0.62 (for the primary material) and 0.54 (for the variant material). This trend is consistent with the differences in specific surface area: the primary material has a higher surface area (45.0 m^2/g) compared to the variant (33.5 m^2/g), and is thus expected to expose a larger number of undercoordinated surface sites where oxygen can reside either as chemisorbed species or as lattice oxygen adjacent to vacancies. The enhanced O_{ads} fraction observed for the primary material indicates both an increased population of chemisorbed oxygen that can contribute to the near surface electron depleted region in ionosorption type descriptions,^{40,41} and with a greater tendency to form vacancy-related, undercoordinated lattice oxygen that can participate in vacancy-mediated Mars-Van Krevelen type oxidation during methane sensing.^{42,43}

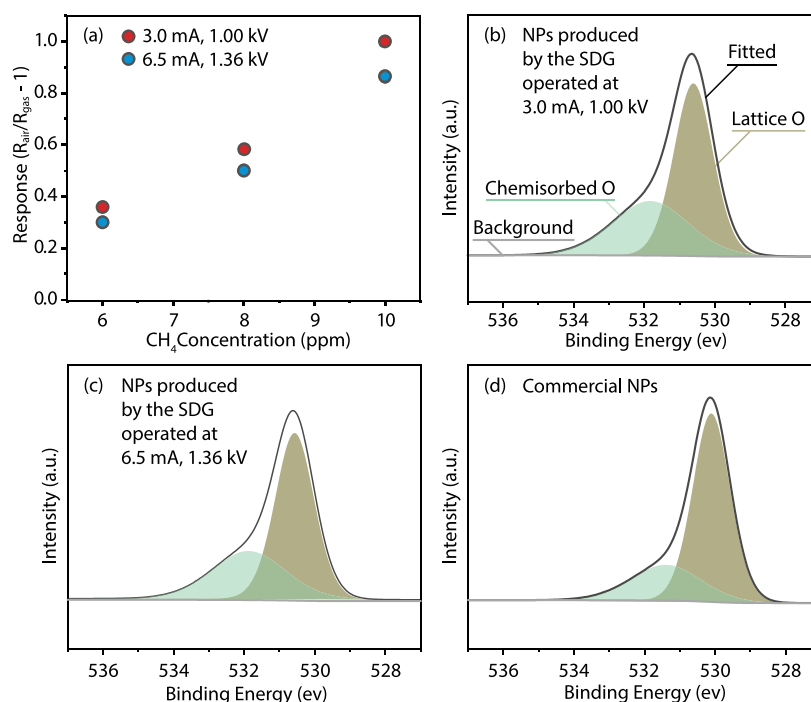


Figure 5. (a) Responses of the primary and the variant sensing materials, prepared with NPs synthesized by operating the SDG at 3.0 mA and 1.00 kV (red circles) or 6.5 mA and 1.36 kV (blue circles), at different CH_4 concentrations. O1s XPS spectra of SnO_2 NPs produced by the SDG operated at (b) 3.0 mA and 1.00 kV, having an $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratio of 0.62, (c) 6.5 mA and 1.36 kV, having an $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratio of 0.54, or (d) available commercially, having an $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratio of 0.36.

Apart from the surface area of the resulting materials, tuning the operating conditions of the SDG also determines the primary and crystallite size of the NP building blocks.²⁰ Size-dependent structural differences are known to influence the amount of chemisorbed oxygen: smaller NPs, having a larger fraction of under-coordinated surface atoms and high-energy facets, typically exhibit a stronger O1s contribution associated with adsorbed oxygen species, while larger NPs show weaker chemisorption-related behavior.⁴⁴ This provides a consistent explanation for the increased adsorbed oxygen observed under the lower-energy conditions used to produce the NPs for the primary materials (i.e., 3.0 mA and 1.00 kV).

We should also note here that the $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratio of 0.62 observed for the primary material is markedly higher than corresponding values typically reported for pure SnO_2 nanomaterials produced by other routes. For example, commercial SnO_2 (see XPS results in Figure 5d) exhibits a ratio of only 0.36, while respective nanofiber (0.47),⁴⁵ nanosheet (0.46),⁴⁶ nanowire (0.34)⁴⁷ and 3D inverse-opal SnO_2 architectures (0.36)⁴⁸ reported in the literature show substantially lower fractions of chemisorbed oxygen species. This comparison highlights a key and previously unrecognized advantage of producing NP building blocks for gas sensing materials by spark ablation: i.e., that the process produces monocrystalline NPs whose surface retains an unusually high tendency to release lattice oxygen for direct reaction with CH_4 , and density of reactive oxygen species, even after annealing. This can most likely be explained by the rapid quenching dynamics of the plasma-driven spark ablation process that can yield clean, defect-rich NPs whose size and surface structure are directly controlled by the discharge energy,⁴⁹ thereby influencing the

amount of chemisorbed oxygen and ultimately the sensing performance of the resulting materials.

In the presence of water vapor, both hydroxyl groups and oxygen species adsorb on the SnO_2 surface and trap conduction-band electrons, forming negatively charged hydroxide and oxygen ions that define the initial electron-depletion layer. Upon exposure of the materials to CH_4 , the gas reacts with the adsorbed hydroxide and oxygen species, releasing electrons back into the conduction band and shrinking the electron depletion layer, thereby reducing the resistance (as shown in Figure 3b). Since O_{ads} species act as dominant electron-trapping centers, materials with higher $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratios, such as those of the primary materials produced here, exhibit stronger resistance modulation and improved methane sensitivity at sub-ppm concentrations.

This is further supported by the data provided in Figure 6, showing how the response of the sensor developed in this work compares to other SnO_2 -based materials, produced by different methods, at wide range of tested concentration of CH_4 . Evidently, the response our sensor has been measured at a concentration down to 0.2 ppm, which is the lowest concentration such sensors have been tested at, and was found to be 1%. For comparison, the response of other sensors that have been tested at CH_4 concentrations from 50 ppm and above^{50–61} range from ca. 7 to 4900%, whereas those tested in the few ppm range exhibit a response in the order of a few percent.^{60,61} All these sensors could in principle have a good enough response when exposed to sub-ppm CH_4 concentrations. However, by extrapolating the response of our sensor to higher CH_4 concentrations (see grey-shaded area in Figure 6), considering the uncertainty of the measurements and an exponential increase of its responses

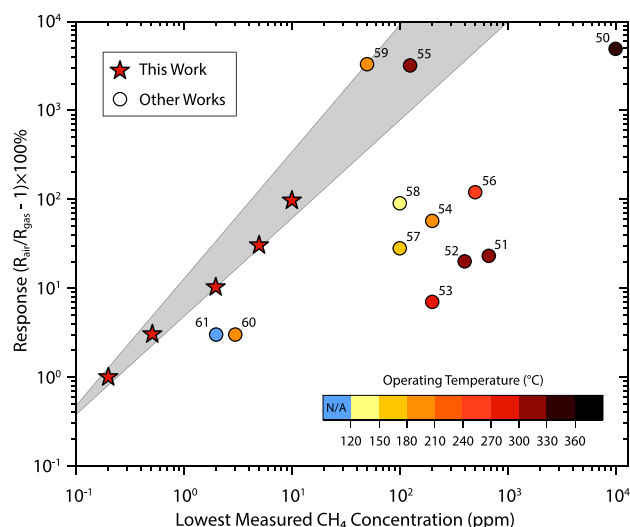


Figure 6. Response as a function of the lowest measured CH_4 concentration that different sensors reported in the literature have been tested at. The numbers next to the circles correspond to the respective references in the literature, while the grey-shaded area indicates the region bounded by our measurements and the best-performing sensors reported in the literature so far.⁵⁹ The response of the commercially available methane sensor TGS 2611-E00 from Figaro Inc.⁶¹ (with unknown operational temperature) is also included for comparison (blue circle).

as a function of concentration, only two of the sensors reported in the literature^{55,59} could possibly meet the performance of our sensors. To investigate that would require additional measurements, which are beyond the scope of this study.

CONCLUSIONS

In this study we investigate for the first time the use of Sn NPs synthesized by spark ablation, which are subsequently annealed to SnO_2 , as building blocks of materials for sensors that can enable ambient monitoring of methane. The NP building blocks, both before and after annealing, were characterized by XRD, BET, and XPS, as well as AFM, SEM, and TEM. The annealed NPs exhibited almost identical physical and crystalline sizes (of ca. 15.0 nm), suggesting monocrystallinity, with an SSA of $45.0 \text{ m}^2/\text{g}$ and an $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratio of 0.62. The sensing materials (in the form of films) were subsequently formed by doctor blading, yielding mesoporous semiconducting structures that demonstrate high response, can reliably detect methane concentrations as low as 0.2 ppm at its optimal working temperature of 275°C , and exhibit excellent consistency and repeatability over many cycles. The theoretical LOD of the films was estimated to be ca. 7 ppb, making them highly sensitive compared to others reported in the literature thus far. The good gas sensing performance can be attributed to the formation of a highly porous network of monocrystalline NPs, the high SSA, and the high population of surface oxygen species. Additionally, the sensor exhibited robust performance across RH conditions ranging from 20 to 80%, providing another reason that makes them ideal for ambient air quality monitoring. Our results also provide evidence of a direct link between the operating conditions used in the SDG to produce the NP building blocks, and the crystal size as well as the SSA of the resulting materials. These, in turn, affect the population of chemisorbed oxygen species on the materials,

providing new insights into how their structural properties affect the sensing mechanism and overall performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssensors.5c02516>.

Measurements that demonstrate the repeatability in the response of our sensor when exposed to a fixed concentration of methane (Figure S1) and XRD and porosity measurements corresponding to the SnO_2 NPs produced by operating the SDG at 6.5 mA and 1.36 kV (Figure S2) (PDF)

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Notes

The authors declare no competing financial interest.

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