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## Environmental sensing semiconducting nanoceramics made using a continuous hydrothermal synthesis pilot plant

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## ABSTRACT

A pilot-scale continuous hydrothermal flow synthesis (CHFS) reactor was used for the synthesis of nanostructured crystalline zinc oxide (ZnO) and indium oxide (In<sub>2</sub>O<sub>3</sub>) materials. The as-prepared oxides were subsequently screen-printed onto metal oxide semiconductor (MOS) sensor substrates and evaluated for their gas sensing performance. Sensing tests were conducted in the range 250–500 °C against -ppb and -ppm concentrations of NO<sub>2</sub> (a hazardous oxidising gas) and ethanol (a reducing gas), respectively. The best performing ZnO material showed a response of 141 towards 800 ppb NO<sub>2</sub> ( $R/R_0$ ) and 80 towards 80 ppm ethanol ( $R_0/R$ ) at an operating temperatures of 250 and 350 °C, respectively. The In<sub>2</sub>O<sub>3</sub> sample exhibited a response of 126 towards 800 ppb NO<sub>2</sub> and 46 towards 80 ppm ethanol at 250 and 350 °C, respectively. The as-prepared powders were characterised using transmission electron microscopy (TEM), Powder X-ray diffraction (PXRD), Raman spectroscopy, BET (Brunauer–Emmett–Teller) surface area measurements and scanning electron microscopy (SEM). The study established the use of a new and scalable synthesis technology for the production of nanoceramics and their use in MOS gas sensing in environmental monitoring as well as potential bio-sensing applications.

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## 1. Introduction

The enhanced gas sensing characteristics of nanosized materials was demonstrated by Yamazoe in 1991 [1]. Very high surface area materials, can promote more surface reactions, therefore can dramatically improve the response characteristics of sensor devices [2,3]. Materials design for sensing applications is a subject of academic and commercial interest [4], particularly with nanomaterials, where there lies the possibility of developing new sensors with interesting 1D particle morphologies, e.g. nano-ribbons, wires and belts [5] and sensor functionalities such as enhanced sensitivity and selectivity.

Previous reports in literature [6,7] have established Continuous Hydrothermal Flow Synthesis (CHFS) as a promising technique for the production of nanostructured In<sub>2</sub>O<sub>3</sub> and ZnO as new materials

for high performance metal oxide semiconductor (MOS) gas sensing. The CHFS production method enables the production of large quantities of materials in hours with the ability to adjust the physical parameters of the synthesis conditions, such as temperature and pressure, and affect particle characteristics [7,8].

Cars, power plants and combustion engines are a major cause of polluting nitrogen oxides (NO<sub>x</sub>) in the air, such as NO and NO<sub>2</sub> [9,10]. Of these gases, NO<sub>2</sub> is the most toxic, with a Threshold Limit Value (TLV) of 3 ppm [9,10]. The respiratory system is the target system under attack from NO<sub>2</sub>, causing adverse health conditions like asthma, emphysema, bronchitis and eventually heart disease, leading to hospitalisation and premature deaths [11]. The severity of exposure to this analyte, illustrates the importance for the detection of NO<sub>2</sub> in the environment.

Ethanol detection is particularly important in the food and drinks industries. Quality control processes such as the food packing safety is one example where ethanol gas sensors are used [12]. Industrial processes such as fermentation and distillation, can cause the concentration of ethanol to reach toxic levels, with irritation of the eyes, nose and skin, and alcohol poisoning being the possible symptoms, depending on exposure levels [13]. 1000 ppm is

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the maximum concentration of acceptable ethanol exposure in a work place [13]. This VOC (volatile organic compound) is also a key biomarker for detection of alcohol content from breath samples of drunk drivers [14] and is therefore key in road safety control and regulation.

Herein, we present a gas sensing study of pilot plant CHFS reactor made ZnO and In<sub>2</sub>O<sub>3</sub> nanomaterials and their evaluation against NO<sub>2</sub> and ethanol at -ppb and -ppm concentrations, respectively.

## 2. Materials and methods

### 2.1. Materials syntheses

Nano ZnO and In<sub>2</sub>O<sub>3</sub> materials were fabricated using a recently commissioned [15] pilot scale CHFS reactor, which was a 20× volumetric scale up process of an analogous laboratory process. Detailed information, which includes the rig schematic [7] and information on the CHFS process, the rig's construction and authentication can be found in relevant literature [15–17]. For the syntheses of ZnO, zinc (II) nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) (Sigma Aldrich) and potassium hydroxide pellets, 85% (Alfa Aesar) were used. For the synthesis of In<sub>2</sub>O<sub>3</sub> nanoceramics, indium (III) nitrate monohydrate [In(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O] (Alfa Aesar) was used. In all cases 10 MΩ deionised water was used.

ZnO nanoparticles were produced in a CHFS pilot plant by reacting a supercritical water flow (400 mL min<sup>-1</sup>) issuing from pump 1 (P-1) at 450 °C, 240 Bar with an ambient temperature flow of precursor solutions, in a confined jet mixer (CJM) [15,18]. Two precursors were used; one issuing from pump 2 (P-2) (zinc nitrate aqueous solution) pre-mixed with another issuing from pump 3 (P-3) (KOH aqueous solution), both at 200 mL min<sup>-1</sup>, yielding a reaction point temperature of 335 °C. When precursors and supercritical water are fully mixed in the CJM, rapid hydrolysis and dehydration of the zinc salt lead to the formation of nucleates with minimal growth. After formation in the CJM, the particles were cooled in flow and after passing through a back-pressure regulator used to maintain a pressure of 240 Bar, were collected as a slurry at the end of the process. The slurry was cleaned by centrifuging (4500 rpm) then decanting and replacing the supernatant with clean deionised water, ensuring to shake each time to re-disperse the solids. This centrifugation process was carried out a minimum of three times until the supernatant was close to neutral, indicated by pH indicator paper.

In<sub>2</sub>O<sub>3</sub> nanoparticles were produced by reacting a supercritical water flow (400 mL min<sup>-1</sup>) issuing from pump 1 (P-1) at 450 °C, 240 Bar with an ambient temperature flow of a precursor solution, in a CJM. Only one precursor was used issuing from pump 2 (P-2) (Indium Nitrate aqueous solution) pre-mixed with deionised water issuing from pump 3 (P-3), both at 200 mL min<sup>-1</sup>, yielding a reaction point temperature of 335 °C. This resulted in the rapid crystallisation and precipitation of nanosized In<sub>2</sub>O<sub>3</sub> particles. In this case, no other auxiliary reagent or modifier such a base was required, but water was used to balance the flows. The slurry was collected and cleaned via dialysis in visking tubing against a buffer solution of 10 MΩ deionised water.

After cleaning, all slurries were subsequently dried in a freeze drier (Virtis Genesis 35 XL) by slowly heating a sample from -60 to 25 °C, over 24 h under a vacuum of 100 mTorr, generating the final material. In a final step, all materials were ground by hand in an agate pestle and mortar to give out a free flowing powder form before further processing.

Table 1 contains a summary of the synthesis conditions employed for each metal oxide sample.

### 2.2. MOS sensor fabrication

Screen printable inks of the nanoceramic materials were formed through simple manual mechanical mixing with an organic binder/vehicle, ESL 400 (Agmet Ltd.), in an agate pestle and mortar. The metal oxides were subsequently screen-printed, using a DEK 1202 screen-printer, onto individual strips of gas sensor substrates. Gas sensor substrates (Capteur Sensors) were 2 mm × 2 mm wide-gap alumina based chips with inter-digitated gold electrodes, with a gap of 182 ± 15 μm between the electrodes. After screen-printing four layers of each ink, (each print being dried under an infra-red lamp for 10 ± 2 min, before printing a new layer) onto individual strips, individual sensor chips from each strip were taken. All chips were then put into a muffle furnace (Elite Thermal Systems Limited) and heat-treated at 600 °C for 1 h in air to burn off the organic vehicle. Spot welding was then performed on each chip, which required 50.8 μm Platinum wires (0.002 inches in diameter, 99.95% metal basis, Alfa Aesar) to be spot welded to the platinum heater track at the bottom and the gold electrodes on the top of the gas sensor chips, using a Macgregor DC601 parallel gap resistance welder. The chips were then further welded onto individual housings.

### 2.3. Materials characterisation

All materials characterisation, except SEM imaging, was carried out on the as-prepared powder samples. Morphology and particle size of the nanomaterials were investigated using a Jeol JSM-2100 Transmission Electron Microscope using a LaB<sub>6</sub> electron source. The images were taken after creating a dispersion of a particular metal oxide in methanol through gentle ultrasonication and drop coating onto carbon-coated copper grids (Holey carbon film, 300 mesh Cu, Agar Scientific). XRD measurements were taken using a Bruker D4 Endeavour Powder X-Ray Diffractometer using a Cu Kα<sub>1+2</sub> source (λ = 0.15418 nm). Raman spectroscopy was carried out using a Renishaw inVia™ Raman (Renishaw Raman System 1000) microscope using a green argon-ion laser of wavelength 514.5 nm. Brunauer–Emmett–Teller (BET) surface area measurements were carried out using N<sub>2</sub> in a Micromeritics ASAP 2420 instrument with six parallel analysis stations. The samples were degassed at 150 °C for 12 h prior to measurements. Scanning electron microscopy (SEM) images, of the screen-printed and fired powder samples on gas sensor chips, were acquired using a Jeol JSM-6301F field emission scanning electron microscope instrument. All samples were carbon coated prior to SEM imaging.

### 2.4. Gas sensing characterisation

Gas sensing experiments were carried out on an in-house automated test rig [19], which was able to accommodate eight sensors at any one time, placed equidistant around a circular test cell from the centre, where the air/gas inlet was located; thus, allowing all sensors to “experience” the exposure conditions synchronously. The sensors were held at constant operating temperatures via a heater driver circuit connected to each sensor's heater track. Experiments were conducted at a range of operating temperatures in the range of 250 and 500 °C, at 50 °C increments. Sensor conductance measurements were obtained through potentiostat circuits and tested against an oxidising gas: NO<sub>2</sub> in air, (100–800 ppb) and a reducing gas: ethanol in synthetic air, (5–80 ppm). A variety of concentrations of each gas was obtained through dilution of the original concentration with compressed air (79% nitrogen, 21% oxygen). All gases were obtained from the British Oxygen Company. Tests were repeated thrice, to ensure reproducibility, and after a period of three months to assess long term stability.

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