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Journal:	<i>New Journal of Chemistry</i>
Manuscript ID	NJ-ART-06-2022-002709.R2
Article Type:	Paper
Date Submitted by the Author:	02-Aug-2022
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**Zinc stannate microcubes with integrated microheater for low-temperature NO<sub>2</sub> detection**

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**Abstract**

This paper reports a facile technique to construct an oxide nanostructured film on a low-power microheater sensor platform to detect the NO<sub>2</sub> gas with high sensitivity and selectivity at a low temperature. Microcube-shaped zinc stannate (ZnSnO<sub>3</sub>) nanostructures prepared through a co-precipitation method were used to detect NO<sub>2</sub> down to 85 ppb at 110 °C with fast response and recovery time. Specifically, a 192% response in resistance change has been measured for the 5 ppm NO<sub>2</sub> gas with a response time of 3.36 mins, excellent reproducibility, long-term stability, and high selectivity. The good gas sensing performance of ZnSnO<sub>3</sub> microcubes is the result of its porous surface, which provides a large surface area and suitable absorption-desorption processes. The versatility of ZnSnO<sub>3</sub> nanostructures may be further exploited with various sensing units on a single chip towards the development of arrays as in electronic noses.

**Keywords:** Zinc Stannate; Microcubes; NO<sub>2</sub> sensor; Microheater; Gas Sensor

## 1. Introduction

Chemiresistive gas sensors made with metal oxide semiconductors (MOS) on ceramic substrates have been widely used to detect hazardous gases in industrial factories and commercial spaces to monitor air quality [1]. However, state-of-art sensors used in the fields are bulky and costly with high power consumptions ( $\sim 500$  mW), which makes them unsuitable for portable and battery-powered devices as a heater is needed to boost the sensitivity and response/recovery rates [2,3]. To overcome these limitations, miniaturization with microfabrication techniques has been employed to produce small and low-cost devices with low power requirements [3]. Nanostructured metal oxides with large surface areas and porous structures have been proposed to increase sensitivity, including microspheres, microcubes, and nanocages with facile adsorption-desorption processes [4–8]. The choice of nanostructured metal oxides is usually determined by the target gases. For instance, various metal oxides/binary oxides have been investigated including ZnO, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub> [9–12]. The primary challenges with gas sensor devices are selectivity and operation temperature. Researchers are particularly interested in room temperature operation and there have been numerous attempts to increase the selectivity of these sensors. The selectivity towards a specific analyte can be enhanced by adjusting the surface-to-volume ratio, grain orientation, and film morphologies [13–15]. Other reported methods include substitutional doping, the formation of composites and hybrids with other nanomaterials such as metal oxides, 2D materials, carbon nanotubes, and so on, as well as chemical functionalization with noble metal nanoparticles. For example, Ma et al. [16] reported 3D SiO<sub>2</sub>@MWCNT core-shell nanospheres for highly sensitive nitrogen dioxide (NO<sub>2</sub>) gas detection at room temperature with best sensitivity of 82.61%. The response time was observed 25 min. and they used UV illumination to achieve complete recovery (44 s). Similarly, Zhang et al. [17] synthesized In<sub>2</sub>O<sub>3</sub> NWs using electrospinning and reported a high sensing response of 740 at 5 ppm NO<sub>2</sub> in the dark at room temperature. However, they utilized visible light irradiation to shorten the recovery time (20 s). Huang et al. [18] developed a robust NO<sub>2</sub> sensor using SnS<sub>2</sub>/rGO nanohybrids, showing a 650% with response time 75 s at room temperature and achieved complete recovery under visible light region. UV-light has been utilized to increase the performance of oxide and 2D materials-based gas sensors. However, UV-light degradation to the structure of the material can significantly impair reproducibility [19].

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3 Nitrogen dioxide ( $\text{NO}_2$ ) is an air pollutant with a pungent odor and high toxicity generated  
4 from fossil fuels in the combustion processes and chemical plants [15]. Overexposure to this gas  
5 can cause respiratory problems, which is particularly harmful to people with asthma [20–22]. The  
6 National Institute for Occupational Safety and Health (NIOSH) has set 1 ppm and a 15-min short-  
7 term limit as the emission standard [23]. The demand for sensitive and selective gas sensors to  
8 detect  $\text{NO}_2$  with low power consumption has sparked sensor research with aforementioned metal  
9 oxides, but most of these materials have limitations in terms of operating temperature and  
10 selectivity [9,24,25]. Binary metal oxides are those that contain at least one transition metal ion  
11 and one or more electrochemically active/inactive ions. However, as compared to single-  
12 component oxides, binary metal oxides may have a higher redox chemical ability and may  
13 integrate contributions from two types of ions to improve sensing performance [26–28]. Zhou and  
14 co-workers [29] synthesized  $\text{ZnSnO}_3$  hollow cubes with high sensitivity and selectivity for ethanol  
15 vapor detections at the ppm level at an operating temperature of 260 °C. Patil et al. [30] reported  
16 sensors made with zinc stannate films with a sensor response of 29.3 for the 40 ppm  $\text{NO}_2$   
17 concentration with fast response and recovery speed at an operating temperature of 200 °C. In the  
18 latter case, the room-temperature operation would be possible with the activation of chemical  
19 reactions under UV-light irradiation. Dabbabi and co-workers used  $\text{ZnSnO}_3$  thin films to detect  
20  $\text{NO}_2$  at room temperature with fast response time but found unstable baseline resistance changes  
21 under UV light irradiation [31].  $\text{ZnSnO}_3$  has also been used for detecting volatile organic  
22 compounds (VOCs) and toxic analytes at low ppb levels, though the operation temperature is a  
23 major concern [32–35].

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40 In this work, a simple fabrication procedure is presented for the synthesis of  $\text{ZnSnO}_3$   
41 microcubes together with a low-power microheater to yield an excellent sensing performance for  
42 the  $\text{NO}_2$  gas. The  $\text{ZnSnO}_3$  microcubes were synthesized using a co-precipitation method and a  
43 subsequent annealing process. They were deposited on a microheater platform to enhance the  
44 sensor response and selectivity for  $\text{NO}_2$  at a low operating temperature. The improved sensing  
45 performance is attributed to the large specific surface area of the microtubes, which allows for fast  
46 gas diffusion to the active sites.

## 47 48 49 50 51 52 53 **2. Experimental Section**

### 54 55 *2.1 Synthesis and Materials Characterization*

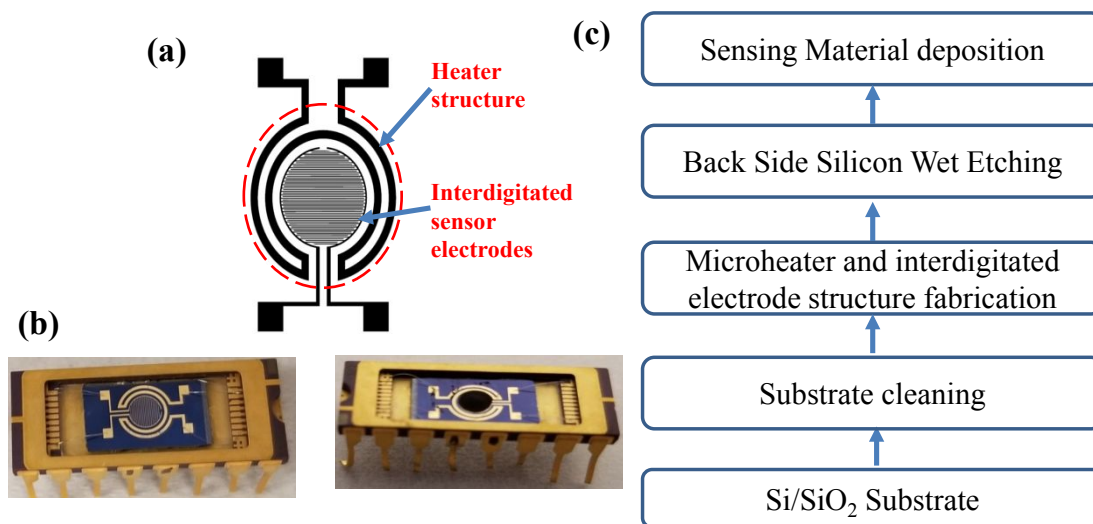
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ZnSnO<sub>3</sub> microcubes were synthesized using a room-temperature co-precipitation method [29]. In a typical synthesis procedure, 0.1M zinc chloride (ZnCl<sub>2</sub>) and sodium citrate (C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>) were dissolved in 10 mL deionized (DI) water and the solution was added to 5 mL of a 0.2 M tin chloride (SnCl<sub>4</sub>) ethanol solution under stirring to form a homogeneous solution. Then, 0.41M NaOH solution (25 mL) was added dropwise into the homogeneous solution and stirred for 1 h. White precipitates of ZnSn(OH)<sub>6</sub> were formed, washed, and centrifuged with water and ethanol for 4 times, and left to dry overnight at 80 °C. The powders were placed in a quartz tube and annealed at 450 °C for 2 h in air with heating and cooling rates of 1 °C min<sup>-1</sup> to obtain ZnSnO<sub>3</sub> cubes. The synthesis procedure is schematically displayed in Figure S1 in the Supporting Information (ESI). All reagents were of analytical grade and used without further purification. The morphology of the samples was characterized using field-emission scanning electron microscopy (FE-SEM, Zeiss Sigma) operating at 5 kV, equipped with X-ray energy dispersive spectroscopy (EDS) for elemental analysis. The crystal structure was characterized using X-ray diffraction (Rigaku, Rotaflex RU-200B) with a Cu K $\alpha$  target ( $\lambda = 0.15406$  nm). The chemical composition and chemical state of the samples were determined with X-ray photoelectron spectroscopy (XPS) using an ESCALAB-MKII spectrometer (UK) with Al K $\alpha$  radiation (1486.6 eV) as the X-ray source for excitation. The pore-size distribution and specific surface area of the samples were estimated using the Brunauer-Emmett-Teller (BET) method based on the nitrogen adsorption-desorption isotherms (BELSORP-mini II, Japan).

## 2.2 Sensor device fabrication and gas-sensing measurements

The gas sensors were fabricated by ultrasonically dispersing as-prepared ZnSnO<sub>3</sub> microcubes (10 mg) in 1 mL isopropyl alcohol. The suspension was then drop-cast onto the microsensor substrate containing a circularly shaped sensing area of interdigitated (line width and spacing of 20  $\mu$ m) encircled by a double meandered Pt heater (line width of 50  $\mu$ m) to regulate the operating temperature and ensure its uniformity as shown in **Figure 1a-b**. For the fabrication process (**Figure 1c**) [36], a 4-inch Si/SiO<sub>2</sub> wafer was used, and the Pt structure was patterned using standard UV Photolithography and lift-off processes. A 10 nm-thick layer of chromium and 90 nm-thick Pt were deposited by physical vapor deposition onto the wafer. The metal lift-off was performed by placing N-methyl pyrrolidone at 60-80 °C for 10 min and rinsing it with 2-propanol before drying. Each 4-inch silicon wafer contains 60-70 microsensor electrodes. The electrodes on the silicon wafer

were diced and fixed onto ceramic packages by using a conductive silver paste. The substrate has a circularly shaped sensing area of interdigitated Pt electrodes with 20  $\mu\text{m}$  spacing that is encircled by a Pt heater to regulate and ensure uniformity of the operating temperature. The  $\text{ZnSnO}_3$  solution was drop cast on the active area of microsensors and heated at 90°C for 15 min to evaporate the solvent, followed by calcination at 400°C in an electric furnace in the air for 2 h to stabilize the sample before the gas sensing measurements. Photos of the system are shown in Figure S2. The microsensor electrode was wire-bonded in a ceramic package and placed in a sensor chamber for electrical measurements.



**Figure 1.** a) Schematic illustration of the sensor device. b) Zinc stannate microcubes with and without integrated microheater sensor (c) Microsensor Fabrication process

The  $\text{ZnSnO}_3$  sensor was exposed to various gases, namely  $\text{CO}_2$  (2000 ppm in  $\text{N}_2$ ), formaldehyde (20 ppm in  $\text{N}_2$ ),  $\text{NO}_2$  (21 ppm in  $\text{N}_2$ ),  $\text{H}_2$  (5% in  $\text{N}_2$ ),  $\text{CO}$  (500 ppm in  $\text{N}_2$ ), which were calibrated and supplied by Praxair, Inc. A LabView-controlled gas delivery system was used to control the total flow rate of 300 sccm to the sensor chamber. The sensor signal was analyzed using a data acquisition system (Labview) with an open-source Java-based instrument (Zephyr) for controlling and obtaining the data [37–39]. The sensor measurements were conducted with a Keithley 2602 source meter by applying a bias voltage and recording the current, from which the resistance  $R$  was calculated. The gas sensing parameters obtained were the sensor response, defined as  $S = (R_g - R_a)/R_a * 100$  where  $R_g$  and  $R_a$  are the resistance of the sensor film under the exposure to the test gas and fresh air, respectively. The response time ( $\tau_{\text{res}}$ ) is defined as the time

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3 to reach 90% of the full response after the exposure to the target gas. The recovery time ( $\tau_{\text{rec}}$ ) is  
4 defined as the time to return to 10% of the baseline resistance after the target gas flow is stopped.  
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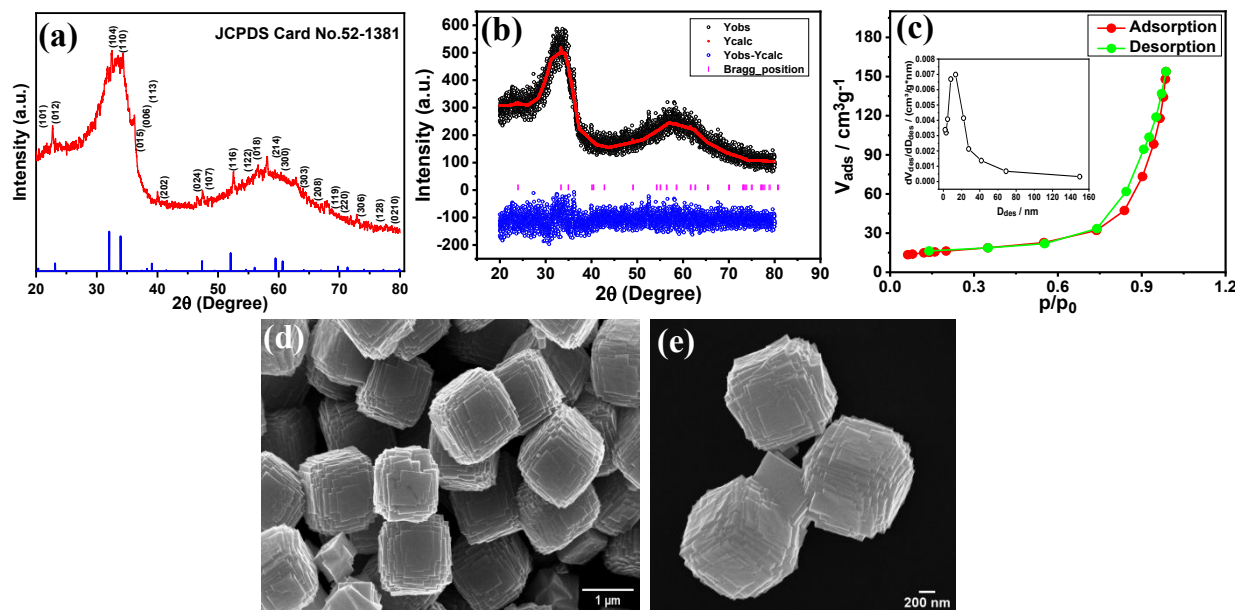
### 7 **3. Results and discussion**

#### 8 *3.1 Microstructural and structural characterization*

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10 Phase identification was performed using the X-ray powder diffraction (XRD) method with the  
11 diffraction pattern in **Figure 2a**. The crystal structure of  $\text{ZnSnO}_3$  in **Figure 2b** was refined using  
12 the Full Proof Rietveld analysis program. The XRD data for the refinement was collected at room  
13 temperature in the  $2\theta$  range from 10 to  $100^\circ$  with a step size of  $0.01^\circ$ . Peak profiles were fitted  
14 with the pseudo-Voigt function.  $\text{ZnSnO}_3$  crystals have a rhombohedral crystal symmetry in the  
15  $R3c(C3v)$  (Space group no. 161) crystallographic point group, where the Sn atom sits at the origin  
16 [40,41]. The structural parameters from the Rietveld analysis are listed in **Table 1**. The absence of  
17 sharp peaks in the diffraction pattern indicated the presence of amorphous  $\text{ZnSnO}_3$ . However, the  
18 Bragg positions from Rietveld refinement were matched with JCPDS file No. 52-1381, confirming  
19 a perovskite structure without impurities. The as-prepared sample showed a pure crystalline  
20  $\text{ZnSn(OH)}_6$  in Figure S3, and this crystalline to amorphous change of the solid microcubes was  
21 observed after calcination at  $450^\circ\text{C}$  for 2 h [29]. Basically,  $\text{ZnSn(OH)}_6$  was dehydrated during the  
22 calcination process, and the original hydrogen-oxygen bonds in the structure were destroyed. This  
23 resulted in a large number of dangling bonds on the surface and disordering the internal lattice,  
24 thus forming amorphous  $\text{ZnSnO}_3$ . Because of the significant number of dangling bonds, the  
25 amorphous  $\text{ZnSnO}_3$  has a larger specific surface area and exhibits superior catalytic activity  
26 compared to that of the crystallized form [42,43]. **Figure 2c** shows the  $\text{N}_2$  adsorption-desorption  
27 isotherms for  $\text{ZnSnO}_3$  microcubes, from which a specific surface area of  $56.3\text{ m}^2\text{ g}^{-1}$  and a pore  
28 volume of  $0.218\text{ m}^3\text{ g}^{-1}$  were calculated. The pore size distribution derived from the desorption  
29 data and estimated from the isotherm using the Barrett–Joyner–Halenda (BJH) model (inset in  
30 **Figure 2c**) indicates a pore diameter ranging from 3 to 92 nm, with an average size of 20 nm. The  
31 morphological features of the  $\text{ZnSnO}_3$  sample are illustrated in **Figure 2 (d and e)**, where the high  
32 and low-resolution FESEM images show uniform microcubes with an average size of 1-1.2  $\mu\text{m}$ .  
33 Elemental analysis and mapping recorded in EDS analysis (Figure S4) reveal the elemental  
34 distribution of Zn, Sn, and O elements without impurities. Notably, the homogeneous dispersion  
35 of the elements was confirmed in addition to Si from the substrate.  
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Table 1: Structural parameters from the Rietveld analysis.

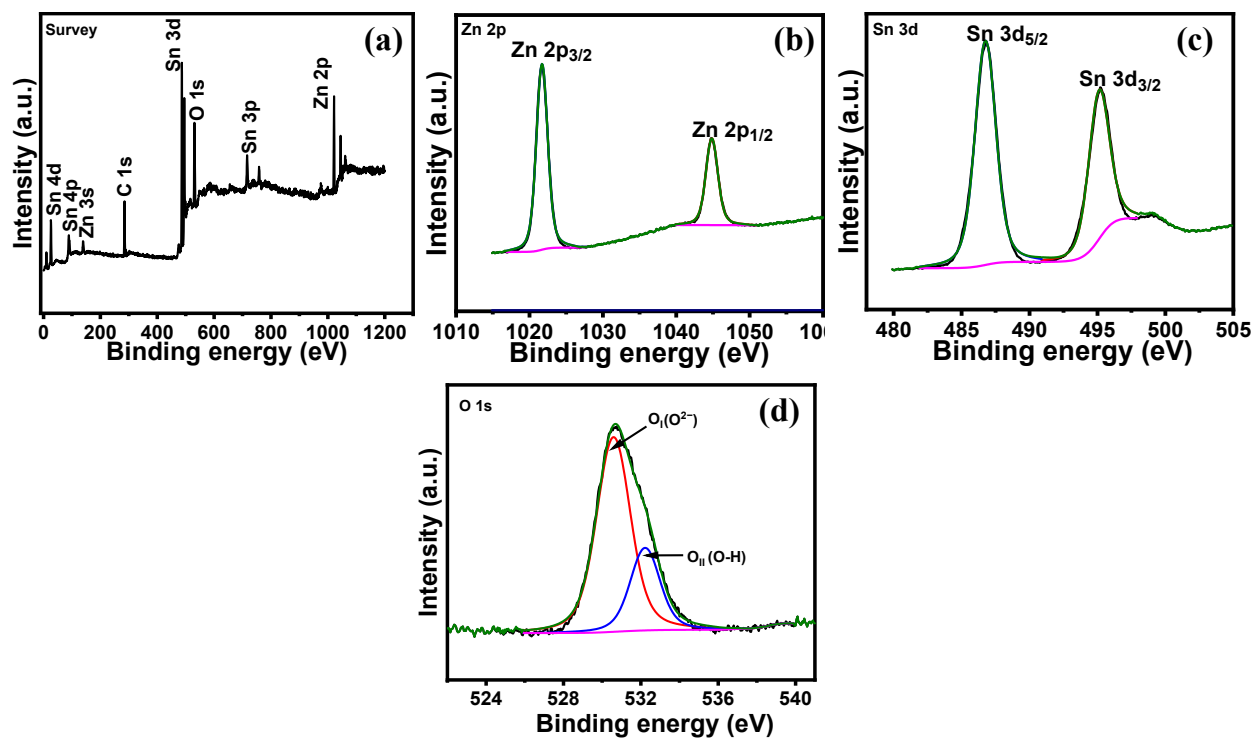
Composition	Lattice constant Å	$c^2$	Zn Coordinates	Sn Coordinates	O Coordinates	Cell Volume
ZnSnO <sub>3</sub>	$a=b=5.1378$ $c=13.4987$	2.01	$x=0.0000$ $y=0.0000$ $z=0.2500$	$x=0.000$ $y=0.000$ $z=0.000$	$x=0.0410$ $y=0.3333$ $z=0.0833$	308.274



**Figure 2** (a) X-ray diffractogram of as-prepared ZnSnO<sub>3</sub> microcubes; (b) Rietveld refinement of ZnSnO<sub>3</sub> sample; (c) Nitrogen adsorption-desorption isotherm of ZnSnO<sub>3</sub> microcubes; (d-e) High- and low-resolution SEM images of ZnSnO<sub>3</sub> microcubes.

The chemical states and chemical composition of ZnSnO<sub>3</sub> microcubes are depicted in the XPS spectra in **Figure 3**. The survey spectrum in **Figure 3a** reveals the presence of Zn, Sn, and O elements, without any kind of impurities. The high-resolution XPS spectra of Zn 2p, Sn 3d, and O 1s after Gaussian fitting are shown in **Figure 3 (b-d)**. Two main peaks of Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub> appear at 1021.6 and 1044.7 eV respectively in Figure 3b [44,45]. The well resolved Sn 3d spectrum in **Figure 3c** features peaks at 494.8 and 486.3 eV assigned to Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub>, respectively, owing to Sn<sup>4+</sup> ions [46]. **Figure 3d** shows the O 1s spectrum, which is deconvoluted into two peaks (O<sub>I</sub> and O<sub>II</sub>). The binding energy 530.6 eV for O 1s is attributed to the metal-oxygen bonding and the other peak at 532.2 eV are due to the oxygen of surface hydroxyl groups (O-H) and chemisorbed oxygen on the semiconductor [45,47,48].



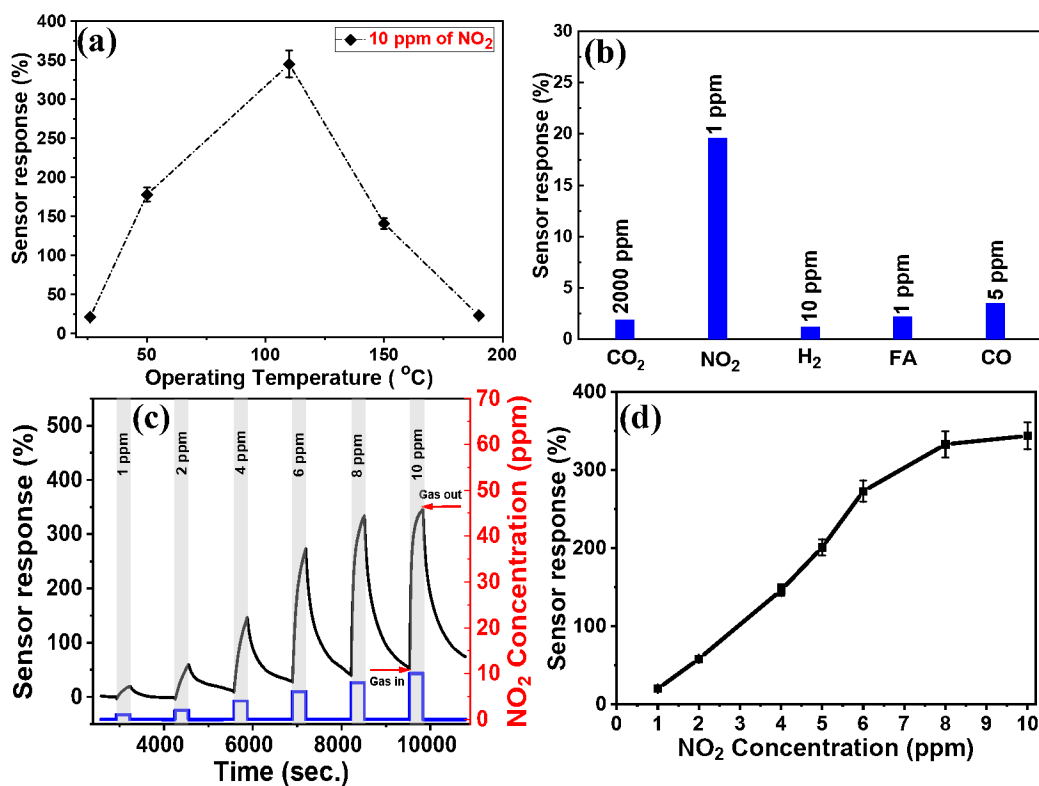


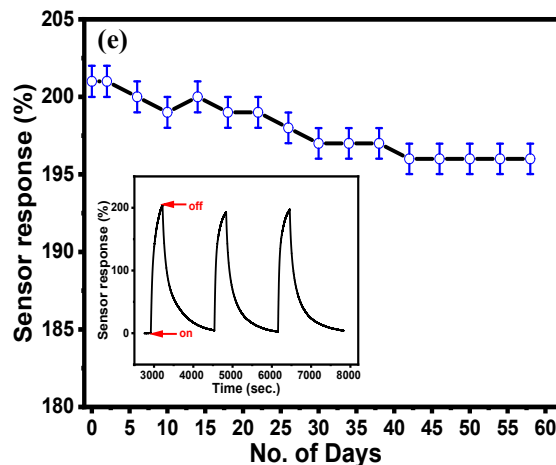
**Figure 3:** (a) XPS survey spectrum; (b) Zn 2p spectrum; (c) Sn 3d spectrum; (d) O 1s spectrum for the ZnSnO<sub>3</sub> microcubes.

### 3.2 Gas Sensing Properties

The gas-sensing performance of ZnSnO<sub>3</sub> microcubes for NO<sub>2</sub> gas is illustrated in **Figure 4**. The operating temperature is known to play a major role in metal oxides because it affects the sensor response/recovery speed via gas adsorption/desorption processes. **Figure 4a** shows the effect of temperature on the sensor response time for the 10 ppm NO<sub>2</sub> (n=4). For the ZnSnO<sub>3</sub> semiconductor, oxygen is adsorbed onto the metal oxide surfaces in the air to attract electrons from the grains forming oxygen species (O<sup>-</sup>, O<sup>2-</sup>, O<sub>2</sub><sup>-</sup>, etc.) between 100 and 300 °C. At low temperatures the reaction rate is low, yielding a low sensor response. With increased temperatures, the thermal energy provided is sufficient to overcome the activation energy barrier for surface reaction, which increases the reaction rate and the sensor response with respect to NO<sub>2</sub>. Above 110 °C, the rate of desorption of chemisorbed oxygen is higher than the reaction rate, thus leading to a decline in response as observed in other works [13]. Hence, the optimum operating temperature (OT) to detect NO<sub>2</sub> is 110 °C. The histogram in **Figure 4b** for toxic oxidizing/reducing gases indicates significant selectivity for NO<sub>2</sub> owing to the rapid reaction rate of NO<sub>2</sub>-molecules on the sensor

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3 surface. **Figure 4c** shows sensing cycles for  $\text{NO}_2$  at  $110^\circ\text{C}$ , with increasing signals for higher  
4 concentrations. The  $\text{ZnSnO}_3$  sensor displays a peak response of 342% upon the exposure to  $\text{NO}_2$   
5 of 10 ppm and 19% for the exposure to  $\text{NO}_2$  of 1 ppm. **Figure 4d** shows the sensor responses of  
6  $\text{ZnSnO}_3$  microcubes with respect to the  $\text{NO}_2$  concentration from 1 to 10 ppm at  $110^\circ\text{C}$  ( $n=10$ ). At  
7 the low concentration region, the sensor response was relatively linear before 8 ppm. This could  
8 be caused by the saturation of sites for adsorption and lack of surface adsorbed oxygen [49]. The  
9 sensor response saturates and reaches maximum after the  $\text{NO}_2$  concentration higher than 10 ppm  
10 (as see the figure 4(d)). Moreover, the threshold limit for  $\text{NO}_2$  gas is 10 ppm, so we varied the  
11 concentration from 1-10 ppm and due to the accuracy of the mass flow controllers in the gas  
12 delivery system, the lowest concentration of  $\text{NO}_2$  that can be reliably delivered was 1 ppm. The  
13 limit of detection is based on the noise level during data collection, more specifically, the noise  
14 level is calculated from resistance of the sensor in air with 10 mins duration. Based on the sensor  
15 response at 1ppm, using a typical signal to noise threshold of 3, the calculated detection limit of  
16 the sensor is about 85.98 ppb. We have also confirmed the reliability and stability of the sensor by  
17 performing sensing experiments until two months without any change in sensor response and film  
18 morphology ( $n=8$ ).





**Figure 4.** (a) Temperature-dependent response of the  $\text{ZnSnO}_3$  sensor exposed to 10 ppm of  $\text{NO}_2$  gas ( $n=4$ ); (b) selectivity plot of  $\text{ZnSnO}_3$  sensor to different oxidising and reducing gases at  $110^\circ\text{C}$ ; (c) dynamic sensing response for  $\text{ZnSnO}_3$ -based sensor to 1–10 ppm of  $\text{NO}_2$  gas at  $110^\circ\text{C}$ ; (d) gas concentration-dependent sensor response of  $\text{ZnSnO}_3$ -based sensor to 1–10 ppm  $\text{NO}_2$  gas at  $110^\circ\text{C}$  by performing number of experiments ( $n=10$ ) (e) Long-term stability tests of  $\text{ZnSnO}_3$ -based sensor with exposures to 5 ppm of  $\text{NO}_2$  gas. The reproducibility of the sensor for 3 cycles of exposure to 5 ppm  $\text{NO}_2$  is illustrated in the inset ( $n=8$ ).

The long-term stability of the sensor was tested for 60 days with 5 ppm concentration of  $\text{NO}_2$  gas at  $110^\circ\text{C}$ . The results in **Figure 4e** show good stability with sensor response gradually lowering from 201% to 196% in 60 days. The reproducibility of the sensor response was confirmed with three successive cycles of  $\text{NO}_2$  at 5 ppm with little changes. Furthermore, it is found that  $\text{ZnSnO}_3$  microcubes can detect 5 ppm  $\text{NO}_2$  with a response time of 3.36 mins while the recovery time is 11.7 mins at  $110^\circ\text{C}$  as shown in Figure S5a-b. Such a high response at low temperatures is rare in the literature, as indicated in **Table 2**. The working temperature of pure  $\text{ZnSnO}_3$  material was observed to be higher because the material requires more activation energy for the detection of  $\text{NO}_2$  gas even at sub ppm levels. Heteronanostructures or surface modified zinc stannate has a higher affinity for oxidizing gases, particularly  $\text{NO}_2$ , favoring trace level detection.

Table 2. Comparison of NO<sub>2</sub> sensing properties for a ZnSnO<sub>3</sub> compound with other materials.

Materials	Concentration (ppm)	Sensor response	Operating Temp. (°C)	Response/Recovery time	Ref.
Zn <sub>2</sub> SnO <sub>4</sub>	40	29.3 <sup>a</sup>	200	8/58 s	[30]
ZnSnO <sub>3</sub>	80	12.05 <sup>b</sup>	RT (under UV-LED)	169/217 s	[31]
Zn <sub>2</sub> SnO <sub>4</sub>	200	2.66 <sup>c</sup>	200	25/326 s	[50]
Pd-Zn <sub>2</sub> SnO <sub>4</sub>	200	3.31 <sup>c</sup>	200	5/179 s	[50]
Zn <sub>2</sub> SnO <sub>4</sub> /ZnO	1	173.26 <sup>a</sup>	300	90/130 s	[51]
Zn <sub>2</sub> SnO <sub>4</sub>	1	102.21 <sup>a</sup>	300	150/160 s	[51]
Zn <sub>2</sub> SnO <sub>4</sub>	5	118.45 <sup>a</sup>	300	100/120 s	[51]
Zn <sub>2</sub> SnO <sub>4</sub>	5	110 <sup>b</sup>	400	NR	[52]
rGO@Zn <sub>2</sub> SnO <sub>4</sub>	5	240 <sup>b</sup>	30	NR	[52]
Pd-ZnO	1	13.5 <sup>a</sup>	100	141/177 s	[53]
Ag-Fe <sub>2</sub> O <sub>3</sub>	4	3.5 <sup>a</sup>	150	NR	[54]
Pt-WO <sub>3</sub>	1	11.24 <sup>a</sup>	150	27/34 s	[55]
ZnSnO <sub>3</sub>	0.8	1.89 <sup>a</sup>	125	NR	[56]
Pt- ZnSnO <sub>3</sub>	0.5	16.0 <sup>a</sup>	125	9/82 s	[56]
ZnSnO <sub>3</sub>	1	19.7	110	40/140 s	This work

Response: <sup>a</sup>(R<sub>g</sub>/R<sub>a</sub>), <sup>b</sup>ΔR/R<sub>a</sub> = |R<sub>g</sub> - R<sub>a</sub>|/R<sub>a</sub>, <sup>c</sup>(R<sub>a</sub> - R<sub>g</sub>)/R<sub>a</sub> <sup>d</sup>Response (R<sub>a</sub>/R<sub>g</sub>),

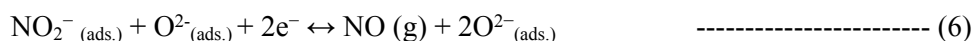
### 3.3. Gas sensing mechanism of ZnSnO<sub>3</sub> microcubes

The findings can be explained with a gas sensing mechanism for ZnSnO<sub>3</sub> microcubes for metal oxide gas sensors [3,35]. The mechanism for ZnSnO<sub>3</sub> microcubes and surface-depletion model for NO<sub>2</sub> gas is illustrated in **Figure 5**. It is a surface-controlled process regulated by the adsorption-desorption in the presence of gas molecules. ZnSnO<sub>3</sub> is a n-type semiconductor oxide in which electrons are the majority charge carriers. When the ZnSnO<sub>3</sub> microcubes are exposed to air as in **Figure 5a**, oxygen is adsorbed to form O<sub>2</sub>, O<sup>-</sup>, O<sup>2-</sup> ion species by trapping/capturing electrons from the conduction band. This decreases the electrical conductivity. At the optimized operating temperature of 110 °C, adsorbed oxygen is mainly present in the O<sup>2-</sup> form. **Figure 5b** shows a schematic diagram of the interaction of O<sub>2</sub> and NO<sub>3</sub> gases with the ZnSnO<sub>3</sub> grain. The reaction kinetics may be explained by the following reactions [57–59]:

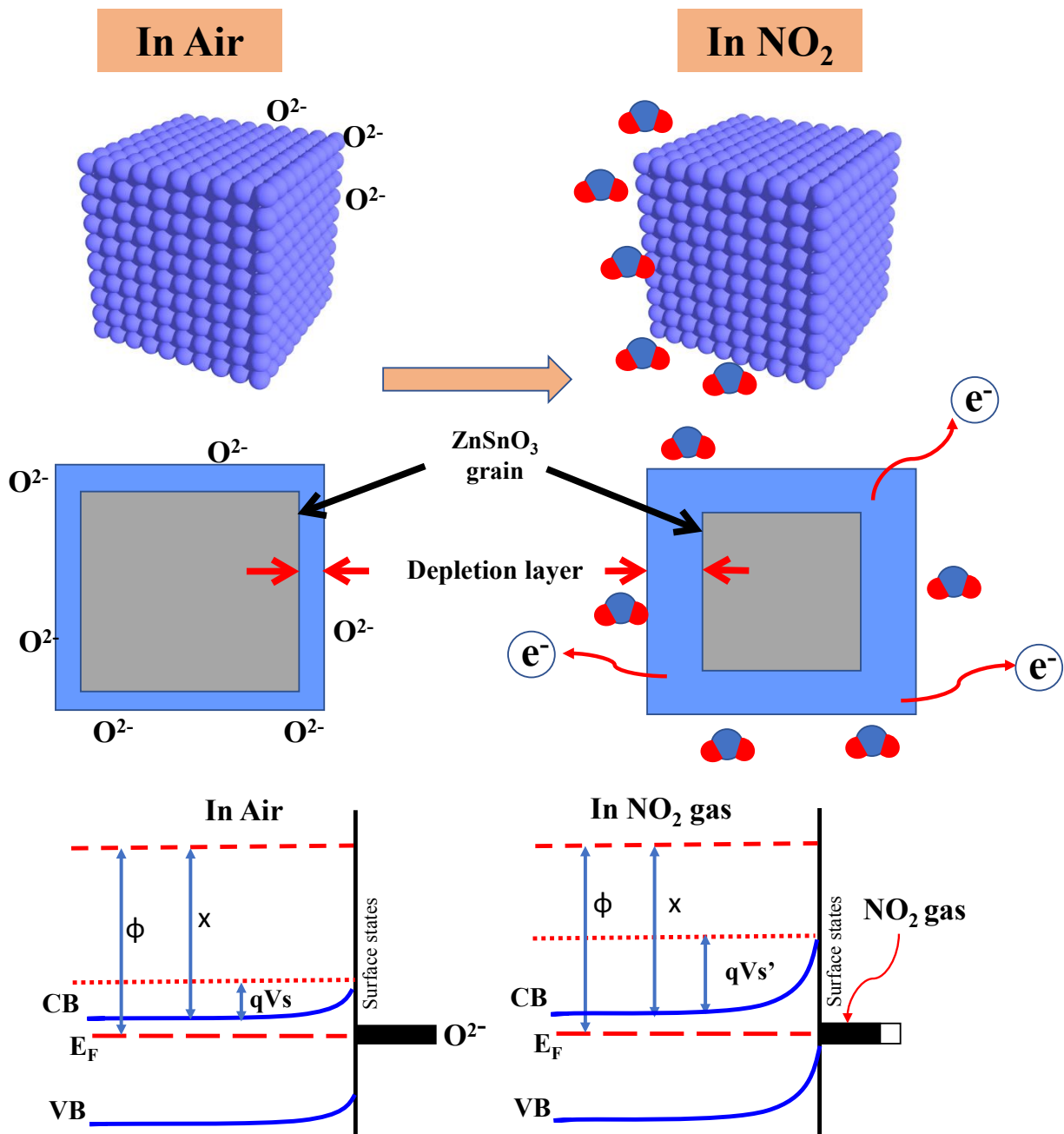




Upon the exposure to  $\text{NO}_2$  gas, gas molecules are absorbed on  $\text{ZnSnO}_3$  microcubes and act as acceptors to attract released electrons, as in the following reactions [60]:



A depletion region is formed on the surface of each  $\text{ZnSnO}_3$  microcube as a result of these reactions, thus causing the sensor resistance to increase. When the sensors are no longer exposed to  $\text{NO}_2$ , resistance values are returned to those in the ambient air owing to a decrease in the depletion layer width and resistance. In other words, extracted electrons are returned to the conduction band, lowering the sensor resistance.

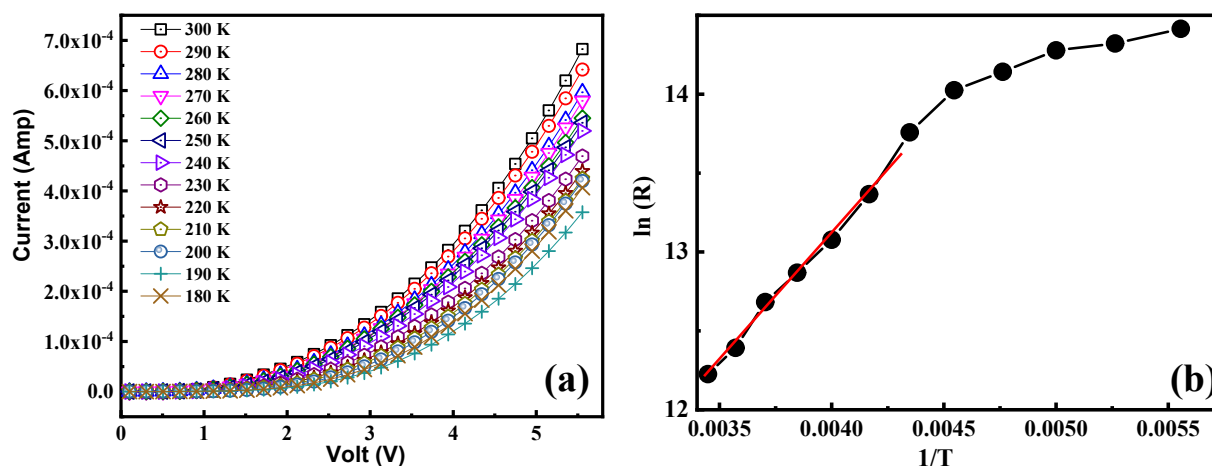


**Figure 5:** Schematic illustration of the  $\text{NO}_2$  sensing mechanism of the  $\text{ZnSnO}_3$  sensor.

### 3.4 Charge transport properties of $\text{ZnSnO}_3$ microcubes

The I-V characteristics of a  $\text{ZnSnO}_3$  film at different temperatures in **Figure 6a** show the current decreases when the temperature decreases as the number of thermally generated charge carriers decreases. The change in resistance (R) with respect to temperature in **Figure 6b** allows for a linear

fitting of  $\ln(R)$  vs.  $(1/T)$  in the range 300-240K, which means that the electrical conductivity of ZnSnO<sub>3</sub> film follows the Arrhenius' law  $R = R_0 \exp\left(\frac{E_a}{kT}\right)$ , where  $R_0$  is a constant,  $E_a$  is the activation energy, and  $k$  is the Boltzmann constant [61,62]. The activation energy was determined as ~1.7 eV using the linear portion of the curve. It is well established that the concentration of the intrinsic charge carriers decreases with the decreasing temperature for semiconductors. Arrhenius' law is expected in the temperature range where intrinsic charge carriers dominate [63]. Because of defects or disordered states in the ZnSnO<sub>3</sub> film at low temperatures, the hopping transport dominates over band transport. This explains the deviation from the Arrhenius plot at low temperatures [64,65]. Taken together, these results confirm the semiconducting nature of ZnSnO<sub>3</sub> films. Moreover, the reported value of work function of Zinc stannate is 5.02-5.03 eV [66,67]. To measure the I-V and gas sensing characteristics, gold electrodes were used as the gold work function is very close to work function of Zinc stannate i.e 5.1 eV [68]. Therefore, gold can make ohmic contact with Zinc stannate.



**Figure 6.** Temperature-dependent (a) I-V characteristics and (b)  $\ln(R)$  vs  $(1/T)$  plot for a ZnSnO<sub>3</sub> film

#### 4. Conclusion and Future Works

We have employed a simple one-step co-precipitation method to fabricate ZnSnO<sub>3</sub> microcubes for the detection of NO<sub>2</sub> on a low-power microheater platform. With the advantages of the large surface area of ZnSnO<sub>3</sub> nanostructures, the resulting sensor shows superior sensing response (average response of ~344 at 10 ppm) to NO<sub>2</sub> with fast response and recovery time at a relatively

low operating temperature of 110 °C. The sensor exhibited excellent stability for a long period of time and high selectivity to NO<sub>2</sub>. This facile and versatile fabrication strategy provides a way to produce low-power gas sensors with low-cost mass productions. We discovered a few limitations in detecting NO<sub>2</sub> with this material, such as operation temperature and selectivity, and even it was observed in published articles [30–32]. The sensitivity is very low at room temperature, with a long recovery time and poor selectivity. Many researchers have used strategies such as surface modification, doping, and light illumination to overcome these issues, which we outlined in the introduction. Future approaches to ZnSnO<sub>3</sub> sensing characteristics could consider various environmental conditions and deep studies to understand the selectivity fundamentals using XPS and XRD characterization. Moreover, the interactions between the sensing layer and gas molecule will be analysed using density function theory (DFT) which will help to overcome the problem of selectivity before the actual experiment. Another possibility is to exploit the versatility of ZnSnO<sub>3</sub> and design different microsensor units with varied responses to produce an electronic nose (E-nose) on a single chip. This could permit overcoming problems of selectivity and operation temperature, as the sensing of NO<sub>2</sub> and other gases would be based on a global selectivity concept.

### Acknowledgements

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05-CH11231, within the van der Waals Heterostructures Program (KCWF16), which provided for gas sensor response characterization. This work was also supported in part by the Berkeley Sensor and Actuator Center (BSAC), an Industry/University Research Cooperation Center. N.J was supported by the Sao Paulo Research Foundation (FAPESP) (grant no. 2014 / 23546-1, 2016/23474-6, 2018/22214-6, 2013/07296-2) and CNPq (Brazil).

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