# Binary sensor prototype for detection of signaling metabolites

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***Abstract*— A portable binary breath analyzer prototype for detection of specific metabolites in breath like nitric oxide, ammonia and isoprene is designed. A binary response implemented with LED display is employed for the prototype. Highly selective $NO$ sensors were fabricated by using modified pervskite based $WO_3$. Experiments demonstrated that the designed prototype embedded with $WO_3$ sensor is able to detect the ammonia gas at a concentration as low as 1 ppm.**

## I. INTRODUCTION

Medical studies have associated certain gaseous constituents of the human breath with specific types of diseases. Hence, chemical sensors capable of detecting these chemical species can be easily used for medical applications. The key deficiency of current sensor/e-Nose technologies is the lack of specificity in recognizing the particular analyte/gas. Three different sensors can be used in the designed prototype to selectively detect hydrocarbons and NOxes. The sensing elements are based on three different types of pure nanostructured metals oxides namely, rutile based $MoO_3 - TiO_2$, modified pervskite based $WO_3$ and monoclinic $MoO_3$. The rutile based elements are selective towards hydrocarbons while the modified perovskite based elements are selective towards nitrogen oxides [1]. The selectivity enables use of simple circuitry for detection and enables design of portable "cut-off" prototype for prescreening patients with specific diseases.

Due to the selectivity of the sensor, pattern recognition algorithms employed with general sensor arrays become obsolete and the conductance of the sensor is directly proportional to specific analyte concentration. Thus to sense the concentration of analyte, the resistance of the sensor is converted to a voltage signal. For a binary response, the percentage increase is compared to a predefined threshold value. The threshold value is set through calibration measurements and the specific LED indicates if the concentration of the analyte has exceeded the threshold value.

In this paper, a highly selective gaseous sensor is first characterized. Then the designed binary sensor prototype for measurement and display purpose is described.

## II. HIGHLY SELECTIVE GASEOUS SENSOR CHARACTERIZATION

$WO_3$ stabilizes in various crystal structures that are all modifications of the cubic $ReO_3$ structure. Of these the monoclinic and the orthorhombic polymorphs are isostructural in that their crystal structures share the same structural elements [2].

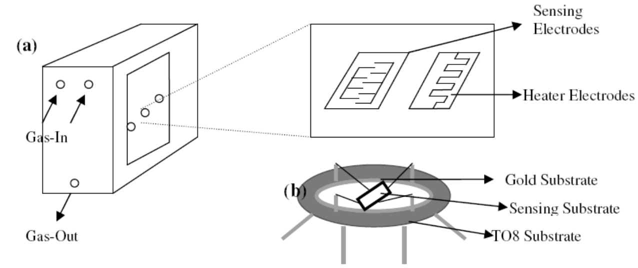

Fig. 1. *(a) Schematic of EOS 835 and the sensing chamber; (b) Schematic of the sensing substrate on the TO8 sustrate*

Sensing experiments were carried out in a modified electronic olfactory system EOS 835 (SACMI IMOLA, Italy). The sensing chamber in EOS 835 can accommodate up to six $3mm$ by $3mm$ sensors at the same time. It is a commercial device that comes along with six $SnO_2$ based sensors that are non-selective. These have been replaced with selective $WO_3$ based sensors. The sensing chamber is made of stainless steel to avoid adsorption/desorption of gases while sensing. The olfactory system has a small pump inside that controls the inlet gas flow. Gas flow was controlled externally by a series of mass flow controllers (MKS 1479A), and the flow was manipulated so that it would match the modified internal flow of EOS 835. A schematic of the sensor on a TO8 substrate, the sensing chamber of EOS 385 and the gas sensing set up are given in Figure 1 and Figure 2.

Experiments with monoclinic and orthorhombic polymorph for different ppb level sensing of $NO$ and $NO_2$ are conducted. Owing to the limitations with the concentrations of the starting gas, the lowest concentration analyzed was 300 ppb. The $NO_2$ and $NO$ sensing response of the monoclinic polymorph is shown in Figure 3 and Figure 4 and the corresponding sensitivity variations are shown in Figures 5 and Figure 6. The sensitivity of the monoclinic polymorph for the same concentration is greater for $NO$ than $NO_2$, although the sensing behavior is very similar.

It is known from previous work [3] that the highest sensitivity towards $NO_2$ in orthorhombic polymorph is attained between 200-300 Celsius degree. The sensing temperature for ppb level analysis was chosen to be 200 Celsius degree.

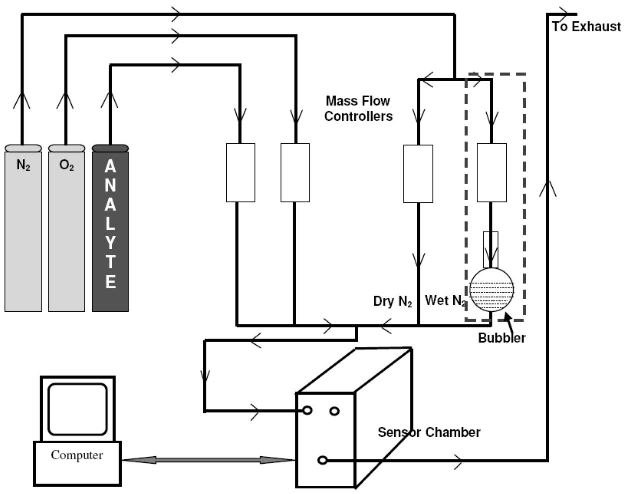

Fig. 2. *Schematic of the gas sensing setup*

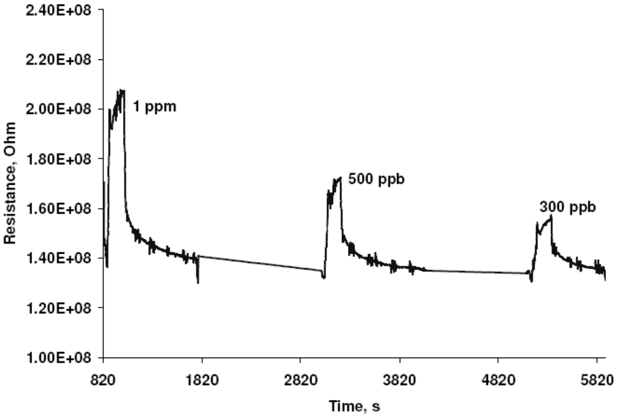

Fig. 3. *Sensing response of monoclinic polymorph at 400 Celsius degree to* $NO$

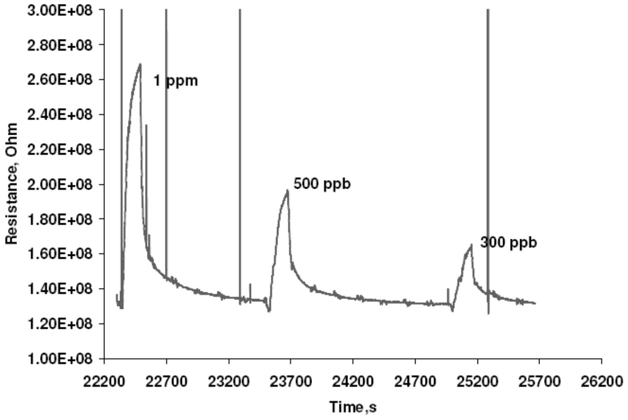

Fig. 4. *Sensing response of monoclinic polymorph at 400 Celsius degree to* $NO_2$

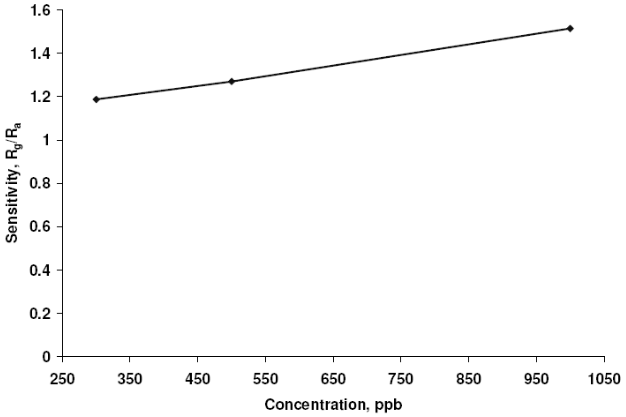

Fig. 5. *Sensitivity variation of the monoclinic sensor with* $NO$ *concentration at 400 Celsius degree*

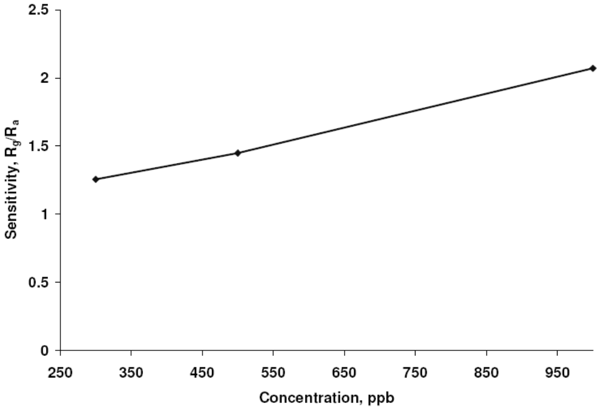

Fig. 6. *Sensitivity variation of the monoclinic sensor with* $NO_2$ *concentration at 400 Celsius degree*

Figure 7 and Figure 8 show the $NO$ and $NO_2$ sensing responses of the orthorhombic polymorph, respectively. The lowest concentration measured for the orthorhombic polymorph is 500 ppb.

TEM analysis was also carried out for both the samples for analyzing both the grain size and crystallographic orientation. Figures 9 and 10 illustrate the low magnification TEM image and selected area diffraction pattern of the $WO_3$ sample heat treated at 515 Celsius degree.

As can be inferred from Figure 9 the grain size ranges from 10-50nm. The agglomeration of the particles is quite typical of sol-gel samples. It can also be seen that the particles form a three-dimensional network, with interconnected porosity. This is again another unique feature of samples prepared by the sol-gel route. The interplanar spacings and the planes indexes correspond to those of orthorhombic $WO_3$ (JCPDS card number 20-1324). Although not observed in the low magnification TEM image, the sample annealed at 515 Celsius degree possesses many crystalline stacking defects known as “crystallographic shear plane” or “Magneli” phases. These are planes of oxygen deficient $WO_6$ octahedra and are visible only

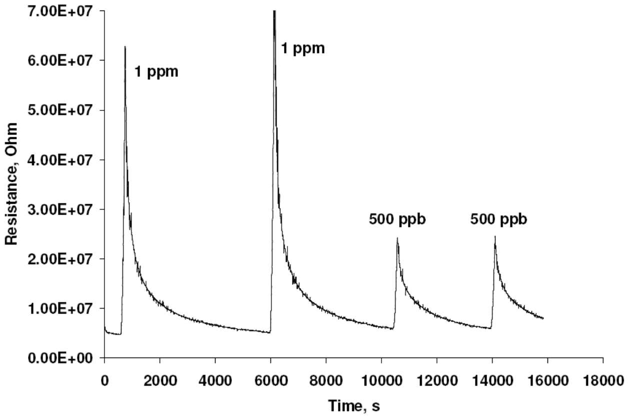

Fig. 7. *Sensing response of orthorhombic polymorph at 200 Celsius degree to* $NO$

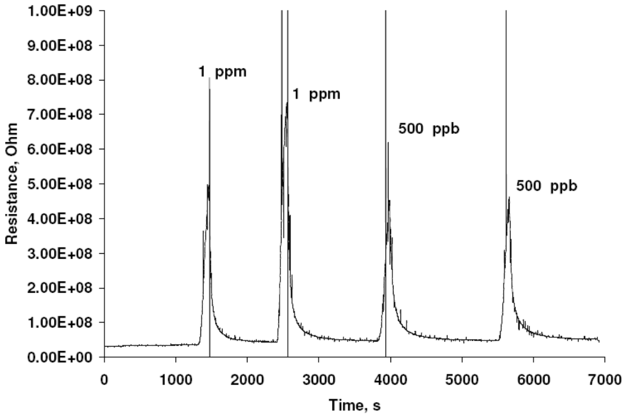

Fig. 8. *Sensing response of orthorhombic polymorph at 200 Celsius degree to* $NO_2$

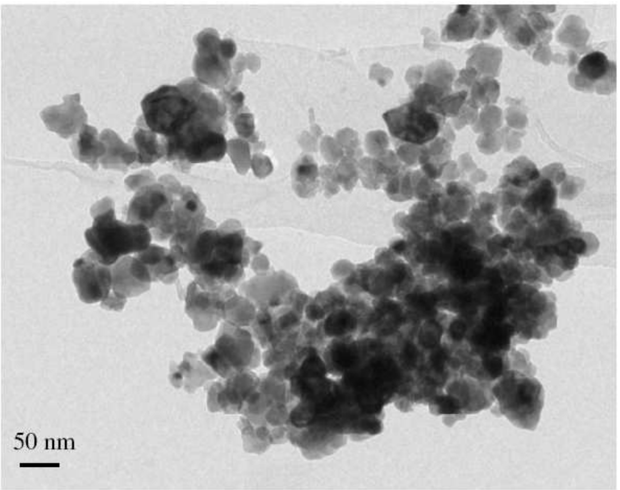

Fig. 9. *General TEM view of the 515 Celsius degree annealed sample*

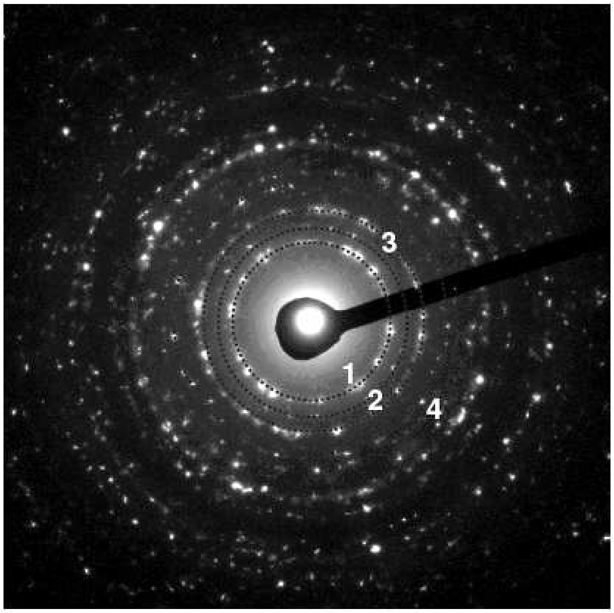

Fig. 10. *SAED pattern corresponding to WO3 sample heat treated at 515 Celsius degree.*

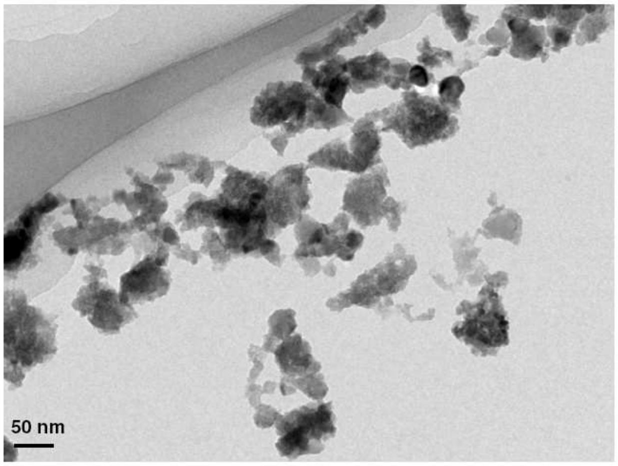

Fig. 11. *General TEM view of the 400 Celsius degree annealed sample*

under high resolution transmission electron microscopy.

The sample annealed at 400 Celsius degree is highly nanocrystalline and hence the SAD rings are broadened as seen in Figure 11 and 12. The average grain size is around 10-20 nm which is smaller compared to the sample heat treated at 515 Celsius degree, which is to be expected because the higher temperature annealing leads to some grain growth as well.

## III. BINARY SENSOR PROTOTYPE

The goal of the designed sensor prototype is to provide measurement and quick 'cut-off' response display. As for the initial design consideration, resolution of the measurement output is not critical. LED display is implemented to indicate the

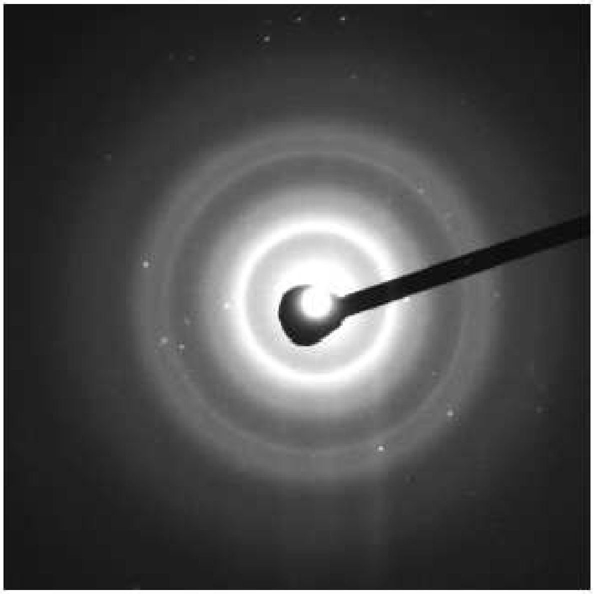

Fig. 12. *SAED pattern corresponding to WO3 sample heat treated at 400 Celsius degree.*

binary measurement results. Thus, when the output resistance is higher than a predefined higher threshold, a red LED is lit up; when the output resistance is lower than a predefined lower threshold, a green LED is lit up; when the output resistance stays in the middle, both LEDs are off.

A schematic of designed prototype is shown in Figure 13. The output of the sensor is connected with a fixed resistor serially. With the help of the voltage divider, the output resistance is converted to a voltage signal, which is proportional to the output signal. The voltage signal, indicated as $Vtest$ in the figure, is connected to a comparator and compared to a threshold voltage, $Vth$, which is created by another voltage divider. A potentiometer is used to create the threshold voltage, so that it is very easy to adjust the threshold. The comparator compares the two inputs and generates a output signal that either turns on or turns off the following LED.

For simplicity, Figure 13 only shows the comparison with higher threshold. If $Vtest$ is higher than $Vth$, the output of comparator is high, thus turns on the red LED. The same schematic is applied for the comparison with lower threshold, where the only difference is $Vtest$ is now connected to the negative terminal of comparator, and $Vth$, which is the lower threshold here, is connected to the positive terminal. In addition, connections for the on-chip heater is also provided in the prototype.

Figure 14 shows a photograph of the designed binary sensor prototype. The prototype is powered with an external power adaptor, and regulated with an on-board adjustable voltage regulator. The adjustable voltage regulator is chosen to enable testing of the sensor with different biasing voltage. The comparators are implemented with commercially available ICs, LM339 from National Semiconductor. Due to the high current, up to 450mA, required from the heater, a heat sink is used to help the regulator work properly.

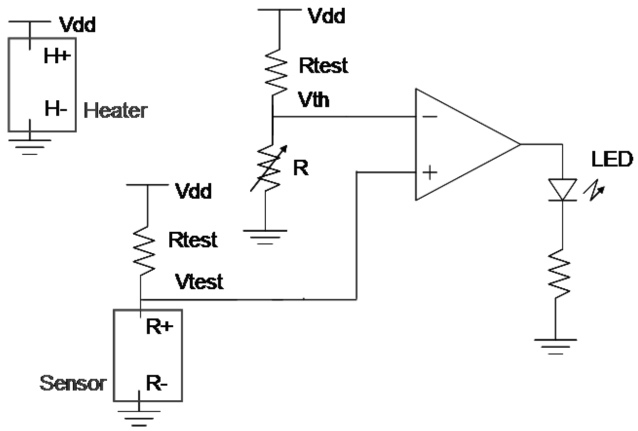

Fig. 13. *Schematic diagram of the designed prototype.*

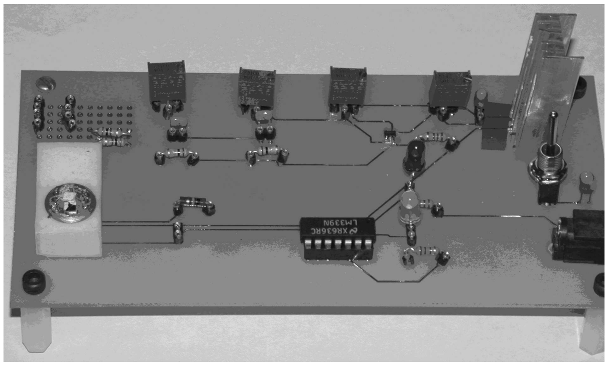

Fig. 14. *Photograph of designed binary portable prototype for detection of signaling metabolites.*

Several experiments were conducted with the prototype. We demonstrated that the designed prototype embedded with $WO_3$ sensor is able to detect the ammonia gas at a concentration as low as 1 ppm, in which case the green LED is lit up.

## IV. CONCLUSION

A portable binary breath analyzer prototype for detection of specific metabolites in breath like $NO$, $NH_3$ and isoprene is designed. We plan to continue with the design of mixed-signal VLSI system that would improve the sensitivity and dynamic range of detection and provide breath analyzer prototype with quantified response.

## REFERENCES

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