Rare Earth Doped Metal Oxide Sensor for the Multimodal Detection of Volatile Organic Compounds (VOCs)

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Abstract

Heated metal oxide sensors have been widely studied for their ability to give a reversible change in the electrical resistance following the interaction with a volatile compound. Another feature is their inherent cataluminescence (CTL) properties when these materials interact with specific volatiles.

This study reports for the first time a zirconium oxide nanomaterial doped with a rare earth metal which gives combined resistance and cataluminescence responses, providing enhanced sensitivity and selectivity of detection via a **multimodal response in a single sensor**. The europium-doped zirconium oxide, $ZrO_2:Eu^{3+}$ was studied and compared with the undoped zirconium oxide, ZrO_2, and tungsten oxide, WO_3. Materials were characterised structurally and tested with a series of volatiles. Both the cataluminescence light emission and the resistance response were recorded at different temperatures (starting from 180°C up to 400°C) and then combined to achieve the dual modality response. Europium-doped zirconium oxide gave a better sensitivity in terms of cataluminescence response than the undoped zirconium oxide sensor; dual modality sensing is demonstrated for ethanol and acetone which give cataluminescence and resistance responses on both the undoped and europium doped zirconia.

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1. Introduction

Interest in the selective detection of volatile organic compounds at low concentrations (VOCs) has increased over the past decade. Detecting VOCs is of crucial importance in different fields such as environmental monitoring[1,2], medical diagnosis[3–5], air quality monitoring [6–8] and industrial safety and security applications[9]. In the case of security applications, the detection of low concentrations (typically ppb levels) of explosives in air has become of increasing interest due to the heightened threat of international terrorism. [10–12]

Among the many detection techniques developed to meet this need, chemical-based sensor systems have a leading role and, in particular, semiconductor metal-oxide gas sensors[13–15]. Detection is typical via a change in their electrical resistance properties allowing high sensitivity but often with limited selectivity. However, this can be improved by doping, the temperature of operation and the use of nanostructured materials. The primary materials studied are typically oxides of yttrium, tin, zinc, tungsten, titanium, and zirconium[16–21].

Another property of a sub-class of metal oxide-based materials that have been utilized albeit, less frequently in sensing applications, is their ability to give chemiluminescence, i.e. light emission as a result of the interaction with a target compound. A particular kind of chemiluminescence, called cataluminescence (CTL) has been reported which arises from the heterogeneous catalytic reaction occurring on the surface of solid catalyst accompanied by light emission[22]. It has been reported that the doping of the metal oxides with certain rare earth metals gives an increase in the production of CTL. In particular, europium, terbium and erbium have been employed successfully to enhance the CTL sensitivity of certain metal oxides such as zirconium oxide [23].

56 Although these sensors display high sensitivity of detection for a range of gases, this

57 aspect is accompanied by a lack of specificity of detection. Another practical issue

58 exhibited by these devices is thus the high false alarm rate, especially when the sensors

59 need to be employed in a real-life environment such as explosives detection[25,26].

60

61 A possible solution, to create a sensor with enhanced selectivity, is via a sensor which

62 simultaneously detects both the light emission (CTL) and the electrical resistance.

63 Another important aspect is the sign of response: (i) the change in resistance can be

64 positive or negative depending on the target gas (oxidising /reducing) or the sensor

65 material properties (n-type/p-type), providing further differentiation between two

66 compounds. (ii) the light emission signal can be positive or absent.

67 Nanoparticle-based sensor systems have shown better performance than those fabricated

68 with non-nano materials. These studies [27–29] have optimised the selectivity of a zinc

69 oxide-based resistive sensor for acetone with respect to ethanol by using dumbbell like

70 zinc oxide nanoparticles and varying the operating temperature. Whilst selective to

71 acetone, the sensor is not able to distinguish between a low concentration of acetone or

72 a higher concentration of ethanol. The addition of a second sensing modality, such as

73 CTL, would facilitate such a differentiation to be made. Thus, this paper reports the

74 tests conducted to determine the best sensitivity and selectivity conditions for detection

75 of acetone (the target) and ethanol (the interferent) for a nano-particle europium-doped

76 ZrO_2 dual modality sensor, as compared with an undoped ZrO_2 sensor and a tungsten

77 oxide sensor, included as a standard resistance-based sensor. Different operating

78 temperatures and different targets and interferents have also been studied. To our

79 knowledge, this is the first report in the scientific literature of such a dual modality

80 sensor based on combined resistance and cataluminescence measurements.

81

82 **2. Methods**

83 2.1 Synthesis of the mixed metal oxide $ZrO_2:Eu^{3+}$

84 The synthesis of the mixed metal-oxide $ZrO_2:Eu^{3+}$, (europium 5 atomic per cent with

85 respect to zirconium) is via a wet chemical method analogous to the one reported in the

86 previous literature[23]. The chemicals utilized for the preparation were of analytical

87 grade and used as received from the suppliers: $ZrO(NO_3)_2$ (Aldrich); $Eu(NO_3)_{3(aq)}$;

88 $NH_4OH_{(aq)}$ (5M) (Fluka).

89 2.5 mL of a 0.02 M $Eu(NO_3)_{3(aq)}$ solution was added to 10 mL of a 0.1 M $ZrO(NO_3)_{2(aq)}$

90 solution and stirred rapidly. 0.1M $NH_4OH_{(aq)}$ was added in a steady stream until the

91 reaction mixture reached pH 8. The precipitate formed was filtered and washed three

92 times with deionised water and the pH adjusted to pH 8 with 0.1M $NH_4OH_{(aq)}$. The

93 precipitate was first dried in an oven at 60°C and finally calcined in a muffle furnace for

94 3 hours at 600°C.

95

96 2.2 Characterization

97 Transmission electron microscope (TEM) images were captured using a Philips CM10

98 TEM, 100kV, with a Gatan Orius SC100 (model 832) digital camera.

99 The metal-oxide nanoparticles were also characterised using a scanning electron

100 microscope (SEM), operating at 30kV, combined with EDX using an FEI Quanta 650

101 field emission SEM. Three different detectors were used: Large Field Detector (LFD),

102 Gaseous Secondary Electron Detector (GSED) and Gaseous Back Scattered Electron

103 Detector (GBSD).

104 The composition of the nanoparticle materials was determined using Energy Dispersive

105 X-Ray Microanalysis (EDX), using an Oxford Instruments AZtec Energy EDX system.

106 The voltage used was between 7.5-20 kV.

107 X-Ray Powder Diffraction (XRD) patterns were recorded on a Bruker D2 Phaser in

108 theta-theta geometry using Cu (Kα1/Kα2 λ = 0.15418 nm) radiation and a Ni Kβ filter

109 (detector side). Additional beam optics and settings: primary and secondary axial Soller

110 slits (2.5°), fixed 0.6mm divergence slit, 1mm anti-scatter-screen, Detector: 1D

111 LYNXEYE with a 5° window, Generator: 30kV, 10mA. The software used for the data

112 analysis was the DIFFRAC.SUITE COMMANDER, Bruker AXS. DIFFRAC.EVA 2.1,

113 Bruker AXS (2010-2012).

114 Vibrational Raman spectra and photoluminescence spectra of sensor surfaces were

115 recorded using a Horiba LabRAM HR Evolution Raman Microscope using an Olympus

116 M Plan x5, NA 0.15 objective lens. For Raman scattering measurements, a 785nm laser,

117 ~30mW, was used. For the photoluminescence spectra, excitation was with a 532nm

118 laser, ~0.3mW.

119 For Cataluminescence and Photoluminescence measurements, the sensor was packaged

120 in a dye cast box with an optical window; vapour samples were input to the sensor

121 chamber to obtain cataluminescence spectra.

122 Cataluminescence spectra were recorded using an EG&G 1460 OMA system including

123 a 0.25m Jarrell Ash 82-497 polychromator, 300 lines/mm grating, and 1254 intensified

124 silicon detector cooled to -20° and an accumulation time of 20 seconds. The sensor was

125 placed immediately in front of the polychromator entrance slit. The experimentally

126 determined black body radiation (BBR) from the heated sensor was subtracted from the

127 total emission spectrum to yield the cataluminescence spectrum.

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130 2.3 Sensor Preparation

131 The sensor substrate was a 3 mm x 3mm square alumina tile. On the sensor (front) face

132 was screen printed two gold interdigitated electrodes (four pairs of interpenetrating bars,

133 electrode gap 100 μm). On the reverse face was a platinum heater track which also

134 served as a temperature sensor. The sensor/heater assembly was wire bonded to a TO39

135 transistor can. The resistance of the platinum heater at different temperatures was

136 determined by placing the sensor in an oven whose temperature could be varied. In

137 operation, a feedback control loop was used to maintain the sensor at the required preset

138 temperature.

139 All the sensors were fabricated using a drop-coating method to apply the sensor material

140 to the interdigitated electrodes: a small amount (0.2g) of the metal-oxide was placed in a

141 glass vial, and sufficient water (0.4 g) was added to produce a thick slurry by stirring.

142 The heater resistance at room temperature was of 10 Ohms. Other resistance heather

143 features are reported in the supplementary information. The sensor was prepared by

144 drop coating the oxide paste on to the top surface of the sensor substrate (3 x 3 mm

145 alumina tile) so that it completely covered the interdigitated gold electrodes. The sensor

146 was then allowed to dry at room temperature for 12 hours before use.

147

148 2.4 Experimental

149

150

151   The sensor was housed in a light-tight chamber of volume 100 mL with input and

152   output tubes (internal diameter of 3 mm). Laboratory air was flowed through the

153   chamber using a KNF-Neuberger micro diaphragm pump at a rate of 100 mL/min.

154   The concentrations were validated by the volatile compounds of interest were diluted

155   from headspace concentrations and then injected into the input air flow using a 10mL

156   gas-tight syringe via a silicone rubber septum attached to the inlet tubing of the sensor

157   chamber. At this constant flow rate, the volatile is input to the sensor chamber and

158   mixed, i.e. diluted, with the flowing laboratory air in a few seconds. The concentrations

159   quoted at the sensor are the diluted values achieved at the sensor surface. Compounds

160   characterised by a shallow headspace concentration (under 1 ppm) were generally

161   heated in a thermostatic oven, and the new enhanced headspace concentration was

162   calculated using the Clausius Clapeyron equation. The concentrations in Table 1 are

163   theoretical values based on the vapour pressure of the test substance. To establish the

164   validity of using diluted headspace concentrations the method was tested using selected

165   ion flow tube mass spectrometry (SIFT-MS). The results of these tests for acetone are

166   reported in the supplementary information. The sensors were tested under ambient

167   humidity conditions (40-60% R.H.)

168   A number of controls were run such as injecting air (at the appropriate temperature) or

169   water headspace to ensure that the response is due to the target and not just due to

170   changes in humidity, background volatiles, syringe contamination or changes in oxygen

171   partial pressure. The dual modality responses for a given sensor were measured at

172   different sensor operating temperatures (150°C to 450°C) and at a range of different

173   concentrations of the target volatile compounds (low ppb to high ppm).

174 The light (cataluminescence) produced following the reaction occurring on the surface

175 of the sensor was detected by a Hammamatsu photomultiplier (HP7820) used in photon

176 counting mode; quantum efficiency ~20%. Output pulses corresponding to incident

177 photons are counted by an ASCEL Electronic AE20401 5.8 GHz Frequency Counter. A

178 650 nm short-pass filter was placed between the sensor and the photomultiplier (see Fig.

179 8(a)) to enhance the ratio of CTL to the black body radiation (BBR) arising from the

180 heated sensor. Generally, three injections of the same concentration of a given

181 compound are made into the chamber, and the cataluminescence response profile was

182 measured.

183 Regarding the resistance, the sensor is connected to a voltage source and the change in

184 current in response to the presence of a volatile compound is monitored via a Keithley

185 Electrometer model 617 and connected through a suitable Picolog: Prologix GPIB-USB

186 (HPIB-USB) analogue to digital converter which is interfaced to a computer running

187 bespoke sensor analysis and signal conditioning software. The applied voltage was of 5 V.

188 For each material was made a single sensor and they have been tested singularly by the dual-

189 modality experiments.

190

191 **3. Results and Discussion**

192 3.1 Materials and Cataluminescence Characterisation

193 Figs. 1(a) and (b) show TEM images of the (a) ZrO_2 and (b) ZrO_2:Eu^{3+}(5%)

194 nanoparticles. Regarding the europium-doped zirconium oxide (Fig. 1(b)) it is observed

195 that some agglomerates formed, possibly caused by uncontrolled coagulation during the

196 precipitation process. The formation of such clusters is more evident in comparison with

197 the undoped ZrO_2, shown in Fig. 1(a). The images also reveal that the nanoparticles are

198 characterized by a narrow particle size distribution and nearly spherical morphology.

199   Average particle size, as calculated by the ImageJ software, was 22 nm for the

200   undoped zirconium dioxide and 15 nm for the europium doped particles. These values

201   are in accordance with those reported in the literature [11].

202   **Fig. 1.a, Fig. 1.b**

203   SEM micrographs are shown in Fig. 2(a) (ZrO_2) and 2(b) (ZrO_2:Eu^{3+}). If the ZrO_2

204   nanoparticles, shown in Fig. 2(a) are compared with the ZrO_2:Eu^{3+} in Fig. 2(b), the

205   formation of clusters is again found for the europium doped material.

206   **Fig. 2.a, Fig. 2.b**

207   The XRD patterns of the undoped ZrO_2 and the europium doped material are shown

208   respectively in Fig.3 and Fig.4.

209   **Fig. 3**

210   **Fig. 4**

211   The Raman spectra are shown in Fig. 5 for the undoped ZrO_2 and the europium doped

212   ZrO_2 materials for excitation at 785 nm.

213   The XRD data are fitted well to a monoclinic phase for the undoped ZrO_2 and the

214   tetragonal phase for the ZrO_2:Eu^{3+} (5%) material.

215   Following the assignment of Hui *et al.* 2015 [30]given in their figure 4, the Raman

216   peaks for the monoclinic and tetragonal phases are indicated in our Fig. 5. Reference to

217   our Fig. 5 confirms that the undoped ZrO_2 and Eu^{3+} doped materials are respectively

218   comprised almost entirely of the monoclinic and tetragonal phases, in agreement with

219   the XRD analysis.

220   It was also possible to calculate the average particle size through the Debye-Scherrer

221   equation $Dc = K\lambda/\beta\cos\theta$ where Dc is the average particle size, K is the Scherrer

222   constant taken to be equal to 0.94, the X-Ray source wavelength is 0.15418 nm, β is the

full width at half-maximum of the peak at a diffraction angle of θ. The average particle

size calculated for the undoped oxide was 17 nm and that for the Europium-doped was

21 nm. These values are in accordance with the values calculated from the TEM images

and those reported in the previous literature [11].

The Energy Dispersive X-ray Analysis (EDX) pattern for the undoped ZrO_2 is shown in

Fig. 6; for this experiment, a voltage of 20kV was used.

Fig. 6

The pattern shown in Fig. 6 identifies the presence of only zirconium and oxygen;

whereas EDX analysis of the ZrO_2:Eu^{3+} material (Fig. 7) shows that effective doping

with europium had been achieved.

Fig. 7

The photoluminescence (PL) spectrum for the ZrO_2:Eu^{3+} material is shown in Fig. 8(c),

recorded at a sensor temperature of 450^OC. The two major PL peaks are at 592 and 607

nm. Hui et al recorded PL spectra for ZrO_2 doped with Eu^{3+} with concentrations in the

range 0.5 to 5%. Reference to figure 7 of Hui et al shows that, for PL excitation at 254

nm, they observed principal PL peaks at similar positions, i.e. 593 and 608 nm; and

when their material was doped with at least 3% Eu^{3+}, their PL lineshapes were similar to

those we found for our europium doped zirconium dioxide.

Cataluminescence spectra are shown in Fig. 8 for the interaction of acetone vapour (2

parts per thousand) with (a) undoped ZrO_2 and (b) ZrO_2:Eu^{3+} also at a sensor

temperature of 450^OC. The cataluminescence spectrum from ZrO_2:$Eu^{3+}$is similar to that

of the corresponding photoluminescence spectrum recorded at the same temperature

246 (Fig. 8(c)). The cataluminescence spectrum from the undoped ZrO_2 is a broad

247 featureless response over the 400 – 700 nm region recorded.

248 **Fig 8**

249

250

251 3.2 Sensing Experiments

252 The following analytes were tested with the apparatus described above: acetone,

253 ethanol, water, hydrogen peroxide, ethylene glycol dinitrate (EGDN), nitroglycerine

254 (NG), 2,4-dinitrotoluene (DNT) and 2,3-dimethyl-2,3-dinitrobutane (DMNB). All

255 chemicals were of analytical grade and used as received from the suppliers. Table 1

256 shows the gas concentration ranges tested. NG and EGDN were in a safe format: 10%

257 by weight immobilised on diatomaceous earth, Kielselguhr (desensitised) and supplied

258 by one of the projects sponsors DSTL. The compounds tested are a mixture of VOCs and

259 other compounds which have been linked to explosives and possible interferents which may

260 limit their detection in specific applications.

261 **Table. 1**

262 The data were collected as sensor response (light emission or resistance change) as a

263 function of time. The cataluminescence response was defined by subtracting the black

264 body radiation from the signal registered by the photomultiplier. The resistance signal is

265 reported as relative resistance $R = R_{gas}/R_{air}$, where R_{gas} is the sensor resistance in the

266 presence of the volatile under investigation, while R_{air} is the value in the presence of air.

267 An overview of the $ZrO_2:Eu^{3+}$ responses, both in terms of cataluminescence and

268 electrical resistance, is reported in Table 2. The operating temperature was of 300°C

269 **Table 2**

270   The dual modality response profiles for the $ZrO_2:Eu^3$(5%) sensor, at an operating

271   temperature of $275^{\circ}C$, are shown in Fig. 9, for three repeat injections of 296 ppm of

272   acetone. The peak responses are seen to be highly reproducible, i.e. $\sim\pm$ 5%, for both the

273   cataluminescence and resistance responses.

274   **Fig. 9**

275   The sensor gives the response simultaneously in terms of light emission and resistance.

276   Referring to Fig. 9, while the response time is comparable for the two different

277   modalities (~10 seconds), the recovery time (1/e) is significantly longer (150 seconds)

278   for the resistance measurement vs the cataluminescence response (~20 seconds).

279   Fig.10a shows the light emission response as a function of the concentration of acetone

280   at an operating temperature of 300°C for the three sensor materials. The zirconium

281   oxide sensor and europium doped zirconia sensor have high cataluminescence

282   sensitivity to acetone at this temperature as compared to tungsten oxide sensor, which is

283   at least an order of magnitude lower.

284   Fig. 10b shows more in detail the zirconium oxide and the europium-doped zirconium

285   oxide response. The europium-doped sensor gives a cataluminescence response which is

286   ~ 5 times that of the undoped zirconium oxide sensor. The convergence at the highest

287   acetone concentrations could be partly due to the saturation of the photon counting

288   system at 10^6 photons per second. This result is consistent with that reported by Zhang

289   *et al*., 2005, where europium doping was seen to improve the light emission and thus

290   the sensitivity of the zirconia cataluminescence sensor, particularly at lower

291   temperatures.

292   **Fig. 10**

14

293   Fig. 11 shows the cataluminescence response at different temperatures for a high

294   concentration of acetone (296ppm) for the tungsten oxide sensor, which does give a

295   measurable cataluminescence response, but only at temperatures above 250°C and

296   concentrations above 30 ppm. The maximum CTL signal is 8000, which is

297   approximately one hundred times lower than for the undoped and europium doped

298   zirconium oxide sensors at this concentration (see Fig. 10(b).

299   **Fig. 11**

300   The sensor performance in terms of selectivity as a function of sensor temperature was

301   also studied. In Fig. 12 the ZrO_2:Eu^{3+} CTL response following the interaction with

302   ethanol (58.7ppm) and acetone (29.6ppm) at different temperatures is reported.

303   **Fig. 12**

304   Fig. 13. shows the ratio of the CTL response to acetone (29.6ppm) to that of ethanol

305   (58.7ppm) for the ZrO_2:Eu^{3+} sensor as a function of temperature. The relative response

306   to acetone (29.6ppm) is higher with respect to ethanol (58.7ppm) despite the lower

307   concentration of acetone at all temperatures. This allows the determination of the

308   optimum operating temperature to obtain maximum selectivity for acetone with respect

309   to ethanol to be identified as 200°C; offering a CTL selectivity for acetone over

310   ethanol, normalized to concentration, of ~20. A low temperature of operation is

311   desirable, and overall, this work has shown that the cataluminescence response is better

312   at lower temperatures when compared to the resistance response.

313   **Fig. 13**

314   Fig. 14 shows the cataluminescence response to nitroglycerine for all three sensors

315   studied. The ZrO_2:Eu^{3+}. showed the best sensing performance for 0.63 ppm

316   nitroglycerine in the temperature range of 250-300ºC. At 350ºC, the cataluminsecence

response is lost in the noise due to the high background signal due to the black body

radiation (BBR). The BBR does limit the use of cataluminescent sensors for low

concentrations at higher temperatures of operation. Whilst europium doping has

significantly increased the CTL signal with respect to undoped zirconia, it has also

shifted the peak cataluminescence response to a higher wavelength where the BBR

signal is higher. Selective wavelength filtering could reduce BBR relative to CTL. For

example, referring to Fig. 8(b), a 50nm width bandpass filter centred around 610 nm

would transmit most of the CTL for ZrO_2:Eu^{3+}, whilst further reducing the BBR.

Fig. 14

The relative resistance response for the three sensors as a function of the concentration

of acetone at an operating temperature of $300^{\circ}C$ is reported in Fig. 15.

Fig. 15

In this case, the WO_3 gives by far the most massive change in resistance while the

zirconium-based sensors give much smaller responses. However, both the undoped and

europium doped zirconia-based sensors do give measurable, albeit smaller, responses as

shown in Fig. 16. This aspect indicates that the undoped zirconia sensor gives a more

considerable resistance change over a wide range of concentrations of acetone when

compared to the europium doped sensor. The main benefit from the perspective of

multimodal sensing is that the undoped and doped sensors do give different response

profiles, showing that the europium doping has affected both the cataluminescence and

resistance responses when compared to the undoped sensor.

Fig. 16

One route to achieving selectivity of detection is to consider the ratio between the

cataluminescence and the resistance responses (CTL/Resistance). In Fig. 17, this dual

modality ratio response is reported for acetone (29.6 ppm) and ethanol (58.7 ppm) at

different temperatures. This graph emphasises that it is possible to get a massive

difference in the CTL/resistance ratio between two compounds, in this case, acetone

and ethanol (target/interferent) at different temperatures. At 200°C, there is a massive

difference, but, at 250°C, the acetone and ethanol ratios are similar. Thus, calculating

the CTL/resistance ratio can be one method of improving selectivity in this multimodal

sensor, with the temperature of operation chosen to optimise differences in this ratio.

Fig 17

Discussion

We believe that this is the first report in the scientific literature of multimodal sensing

combining simultaneous resistance and cataluminescence measurements on the same

heated metal oxide sensor. This work has demonstrated that the approach shows

promise for enhancing the selectivity of detection. In terms of sensor recovery, this is

limited by the resistance response which is much slower than the cataluminescence

response. The selective wavelength of detection combined with dopants other than

europium chosen to shift the CTL to shorter wavelength might offer a route to

increasing the ratio of the CTL signal to BBR noise. This would be particularly useful

for high sensor temperatures and low vapour concentrations, where the high BBR

background limits CTL signal to noise, thereby extending the operational temperature

range for multimodal sensing.

A further approach is to combine a number of multimodal sensors in a sensor array to

offer additional specificity of detection. Such arrays could feature different

nanomaterial sensors operated at different temperatures. Such multimodal micro-

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365   hotplate sensor arrays could be manufactured using MEMS (MicroElectroMechanical

366   Systems) technology. An improved understanding of the CTL and resistance sensing

367   mechanisms could also lead to enhanced sensor design.

368   At present, although all sensors studied gave some cataluminescence in addition to

369   resistance changes, there were considerable differences observed between tungsten-

370   based sensors which were better for resistance measurement and zirconium oxide-based

371   materials which gave enhanced cataluminescence responses and smaller resistance

372   responses

373   For the zirconia material, europium doping was shown to be successful in enhancing the

374   cataluminescence response and modifying the resistance response vs the undoped

375   material. This demonstrates the potential to dope other metal oxide materials to produce

376   multimodal sensors with differing cataluminescence and resistance response profiles.

377   The work presented here represents a new type of sensor with potential to improve

378   selectivity for detection of individual VOCs in the presence of other interfering

379   volatiles.

380

381   There are certain limitations to the study presented. However, work was carried out at a

382   range of sensor temperatures to find optimal response to targets for each sensing

383   modality, more complete environmental testing such as altering ambient temperature

384   and humidity is required. It should be noted that these tests were carried out at a typical

385   room humidity (40-60%RH) and not under dry air conditions. Hence, the sensors show

386   relatively good stability across this humidity range. Moreover, the cataluminescent

387   response is not affected by humidity in the same way as resistance-based sensors. We

388   did not observe any catalumiscent response to high levels of humidity. However,

389 cataluminscent sensors are adversely affected by high temperature, and the baseline

390 light emission rises as the temperature increase, especially marked above 300ºC.

391 However, it should be noted that with better filtering of background light emission vs.

392 Cataluminescent response which are at distinct wavelengths, then this issue could be

393 resolved.

394 Another limitation is the relative cost of combining two modalities compared to typical

395 metal oxide-based sensors which are relatively cheap. The addition of the requirement

396 to measure CTL response adds bulk and a costly photon counting PMT module.

397 However, there are silicon technologies which are appropriate to replace the PMT

398 module and could realise a miniaturised device in future studies. The need for a light-

399 tight cell is also potentially more costly but we have developed field prototypes based

400 on this sensor relatively inexpensively. The baseline resistance of the dual modality

401 sensors giving the best cataluminescent response is relatively high compared to

402 conventional metal oxide sensors. The need to operate at lower temperatures to negate

403 background effects also exacerbates this. However, this paper reports the first step in

404 developing these sensors, and we have tested a range of conventional metal oxide

405 materials, including tungsten that have some CTL based response. Therefore, we

406 envisage the possibility of new materials being discovered with multimodal responses

407 inherent or being synthesised. Future work would consequently, try to identify new

408 materials and also to better understand the sensor characteristics in order to design

409 better and more selective sensors.

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4. Conclusions

We have demonstrated for the first time a multimodal sensor that combines resistance and cataluminescent measurements simultaneously on a single heated metal oxide sensor. We have shown that cataluminescence and resistance measurements can be combined to enhance the selectivity of the sensors to various targets as compared to the single mode sensors.

The systematic screening was undertaken using the ZrO_2, $ZrO_2:Eu^{3+}$ and WO_3 sensors showed that it is possible to create a sensor system with increased selectivity by using the dual-modality. It is thus possible to distinguish between different targets that, even if they gave a similar response under one of the sensing modalities, they could provide a different response to the sensing modality. It is possible to exploit dual modality for enhanced sensitivity to the presence of a target as one of the modalities could be optimised for sensitivity to that target.

In particular, the europium-doped zirconia sensor has shown a better response in terms of CTL even at a relatively low operating temperature, whilst the resistance response is similar to that of the undoped zirconia.. The WO_3 sensor exhibited the best resistance response even with low concentrations of the target compounds but gave limited light emission, which was only detected at high target concentrations. Therefore, it may be considered unsuitable as a multimodal sensor, but its inclusion in a sensor array could be advantageous.

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Captions to Illustrations

Fig.1 Transmission Electron Microscopy (TEM) images for (a) ZrO_2 and (b) ZrO_2:Eu^{3+} nanoparticles.

Fig. 2 Scanning Electron Microscopy (SEM) images for (a) ZrO_2 and (b) ZrO_2:Eu^{3+} nanoparticles.

Fig.3 X-Ray Diffraction (XRD) pattern of the undoped zirconium oxide and relative phase attribution fitting.

Fig. 4 X-Ray Diffraction (XRD) pattern and phase attribution fitting for the ZrO_2:Eu^{3+} material.

Fig. 5 Raman spectrum of undoped ZrO_2 nanoparticles (upper trace) and ZrO_2:Eu^{3+} nanoparticles (lower trace). The positions of peaks are marked for the tetragonal phase (t) and monoclinic phase (m), following Hui et al., 2015; i.e. monoclinic at 179 and 190 cm^{-1} and tetragonal at 147, 264, 319, 462 and 642 cm^{-1}.

Fig 6. EDX spectrum for undoped ZrO_2 material. The peak positions for Zr and O are marked.

Fig. 7 EDX spectrum for ZrO_2:Eu^{3+}. The peak positions for Zr, O, and Eu are marked.

Fig. 8 Photoluminescence and cataluminescence spectra at $450^{O}C$: (a) cataluminescence from undoped ZrO_2 for acetone at 2 parts per thousand (ppth). The dotted line indicates the calculated form of black body radiation (BBR). (b) cataluminescence from ZrO_2:Eu^{3+} for acetone at 2 ppth and (c) photoluminescence from ZrO_2:Eu^{3+} with 532 nm excitation.

Fig. 9 Resistance (upper trace) and Cataluminescence (lower trace) responses from the ZrO_2:Eu^{3+} sensor ($275°C$), for three injections of 296 ppm of acetone.

Fig. 10 Cataluminescence response as a function of the concentration of acetone for (a) the three different sensors on a vertical scale and (b) detail of the ZrO_2 and ZrO_2:Eu^{3+} sensor responses on a logarithmic vertical scale.

Fig. 11 Cataluminescence response for a WO_3 sensor following the interaction with 296 ppm of acetone, at different temperatures.

Fig. 12 Cataluminescence response from ZrO_2:Eu^{3+} as a function of temperature for ethanol (58.7 ppm), lower trace, and acetone (29.6 ppm), upper trace.

Fig. 13 Ratio between acetone (29.6 ppm) and ethanol (58.7 ppm) cataluminescence signals at different temperatures for the ZrO_2:Eu^{3+} sensor.

Fig. 14 Cataluminescence response for the three sensors studied for nitroglycerine (0.63 ppm) at different temperatures.

Fig. 15 Relative resistance (R_{gas}/R_{air}) response as a function of the concentration of acetone for the three different sensors studied at $300°C$.

599 Fig. 16 Relative resistance (R_{gas}/R_{air}) response at 300°C for the undoped zirconium
600 oxide sensor (upper trace) and ZrO_2:Eu^{3+} (lower trace).

601 Fig. 17 Ratio between the relative CTL signal and the relative resistance signals for
602 acetone (29.6 ppm) and ethanol (58.7 ppm), for the ZrO_2:Eu^{3+} sensor as a function of
603 temperature.

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606

607 **Table 1 Volatile organic compounds (VOCs) tested and relative sample vapour**

608 **concentration**

Sample Vapour Concentrations (ppm)	
Sample	Concentrations (ppm)
Acetone	0.00296 – 296
Ethanol	0.005871 – 58.71
Water	312
Hydrogen Peroxide	1.92
Ethylene Glycol Dinitrate (EGDN) 75°C	0.63
Nitroglycerine (NG) 75°C	0.64
2,4-Dinitrotoluene (DNT) 75°C	0.05 – 0.5
2,3-Dimethyl-2,3-Dinitrobutane (DMNB) 75°C	2.76

609

610

611 **Table 2 Cataluminescence (CTL) and electric resistance response for the**

612 **ZrO$_2$:Eu^{3+} sensor, following the interaction with all the VOCs tested at different**

613 **concentrations. Operating temperature of 300°C.**

Compound	Concentration (ppm)	CTL Response (Hz)	Relative Resistance Response (R$_{gas}$/R$_{air}$)
Acetone	296	1.35×10^6	133.90
Acetone	29.6	4.42×10^5	22.67
Acetone	2.96	2.80×10^4	3.99
Acetone	0.296	9.61×10^3	2.04
Acetone	2.96×10^{-2}	1.11×10^3	1.21
Ethanol	58.71	1.64×10^5	18.78
Ethanol	5.871	8.10×10^3	1.88
Ethanol	0.5871	3.17×10^3	1.35
Ethanol	5.871×10^{-2}	914.18	1.10
H$_2$O	312	0	1
H$_2$O$_2$	1.92	0	1
2,4-DNT	0.543	7.14×10^3	1.77
DMNB	2.76	0	1
EGDN	0.631	1.39×10^3	1.15
NG	0.632	1.86×10^3	1.20

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615

200 nm

621

Fig.1a

623

200 nm

624

Fig.1b

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| 5/16/2019 2:57:14 PM | det GSED | HV 30.00 kV | spot 3.0 | mag ⊞ 200 000 x | HFW 1.04 μm | WD 4.3 mm | pressure 4 Torr | ⊢————— 200 nm —————⊣ |

627

Fig. 2a

629

| | 5/17/2019 2:32:29 PM | det GSED | HV 30.00 kV | spot 3.5 | mag ⊞ 200 000 x | HFW 1.04 µm | WD 4.4 mm | pressure 5 Torr | ⊢—— 200 nm ——⊣ |

630

Fig. 2b

632

633

Fig. 3a

635

636

Fig. 3b

637

638

639

Fig. 4a

641

The chart legend reads:
Experimental pattern MF02 Zirconium oxide Eu
Calculated pattern (exp peaks) (Rp=72%)
Background

642

Fig. 4b

644

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Fig. 5

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Fig. 6

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Fig. 7

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Fig. 8

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Fig. 9

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Fig. 10a

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Fig. 10b

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Fig. 11

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Fig. 12

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Fig. 13

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Fig. 14

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Fig. 15

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Fig. 16

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Fig. 17

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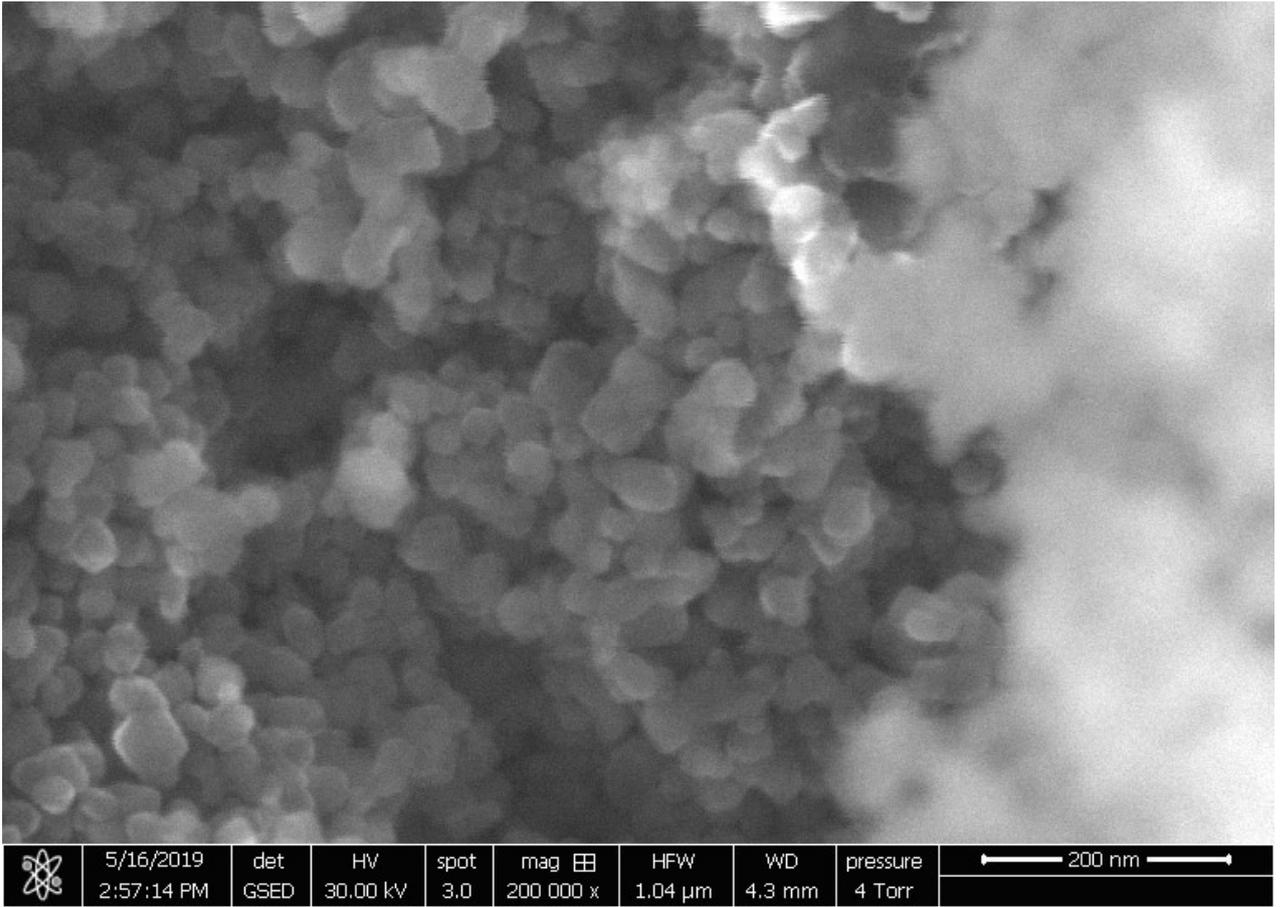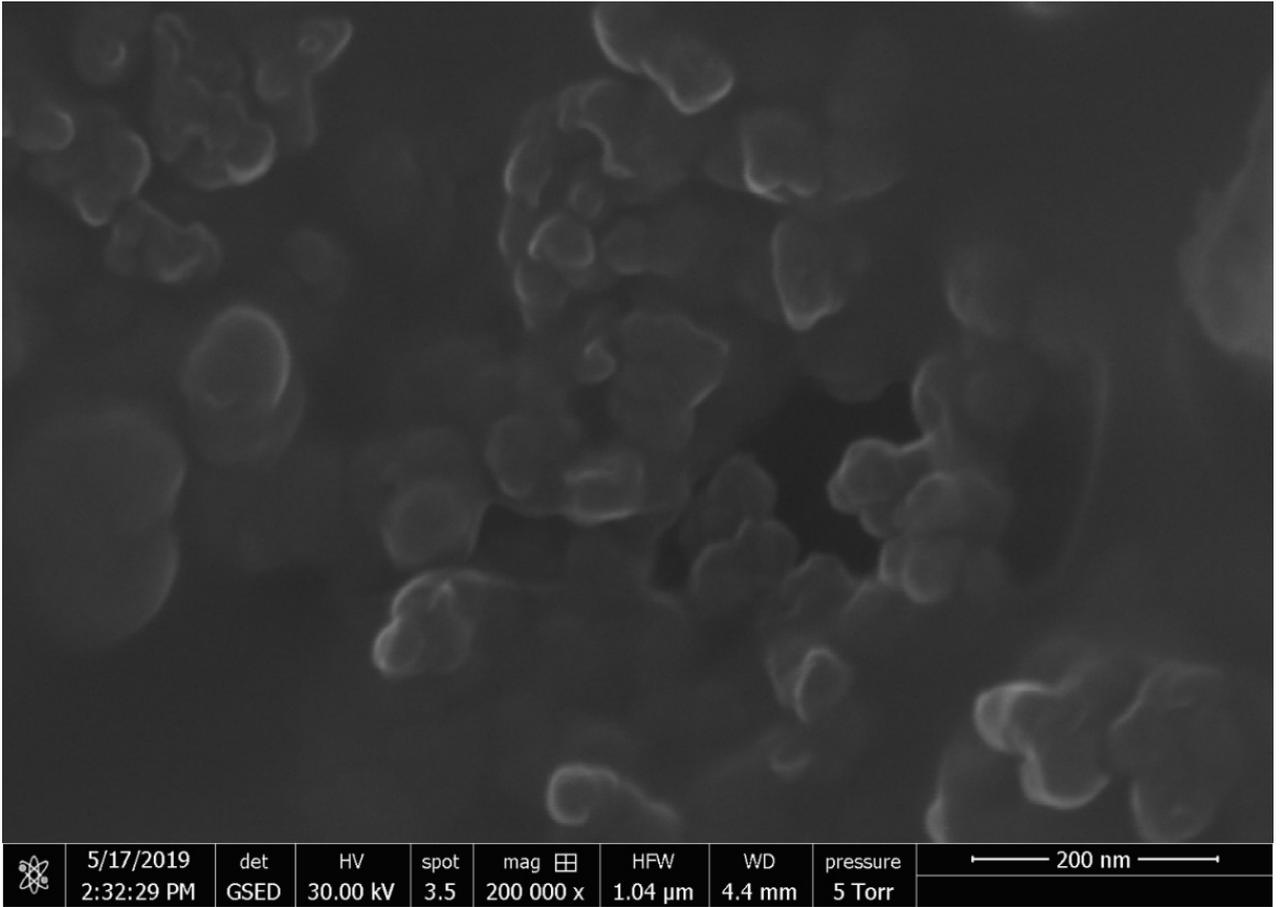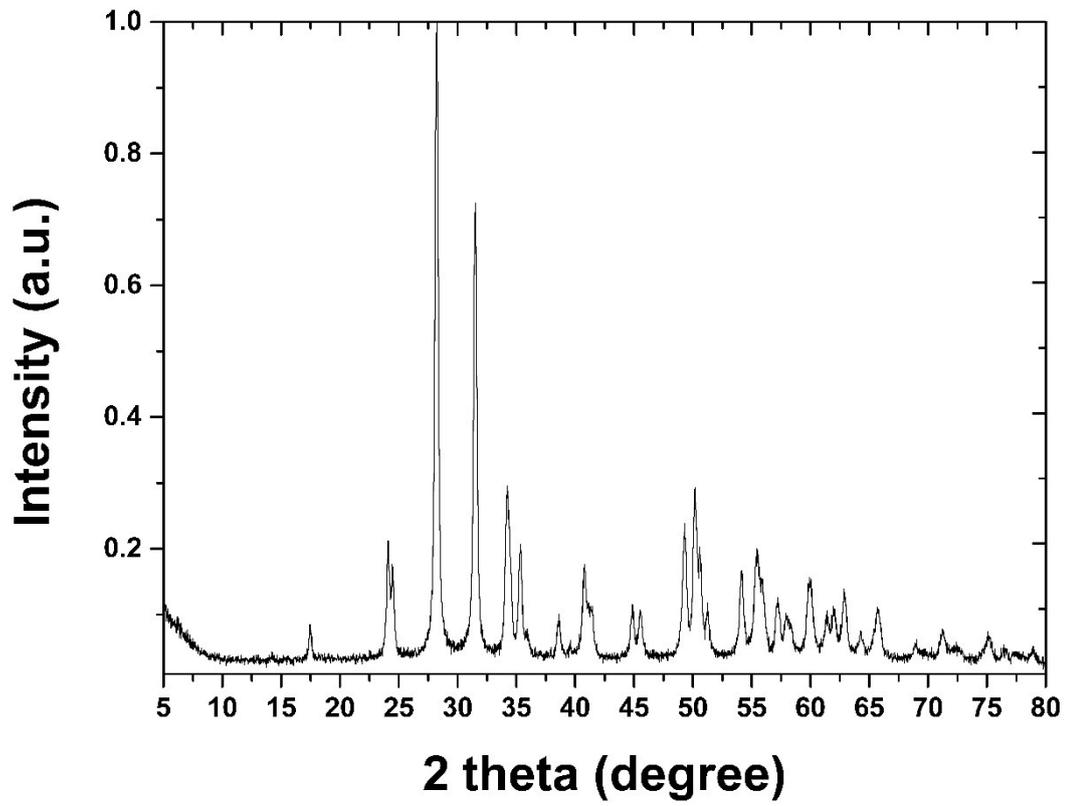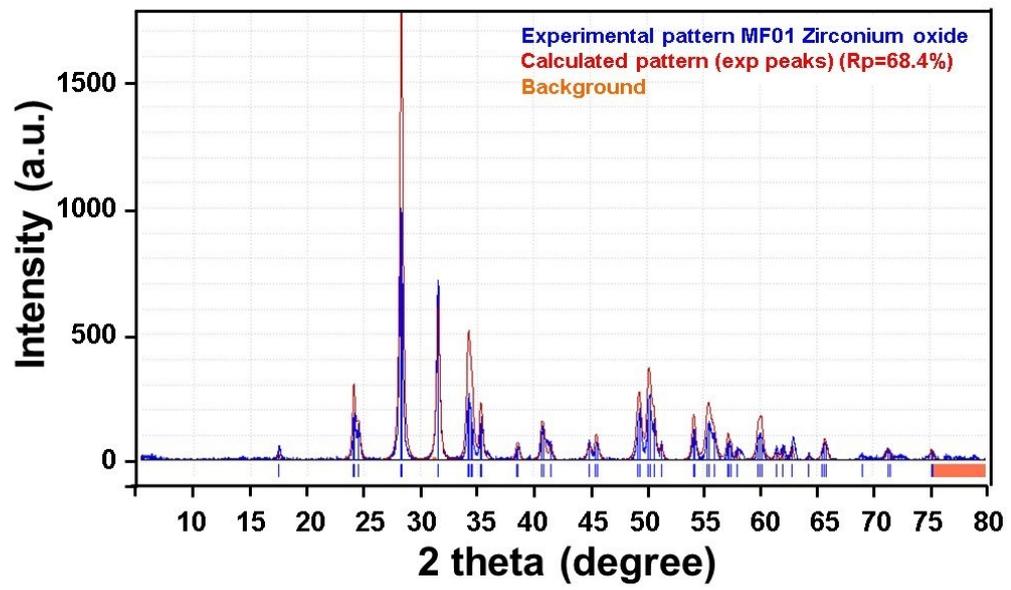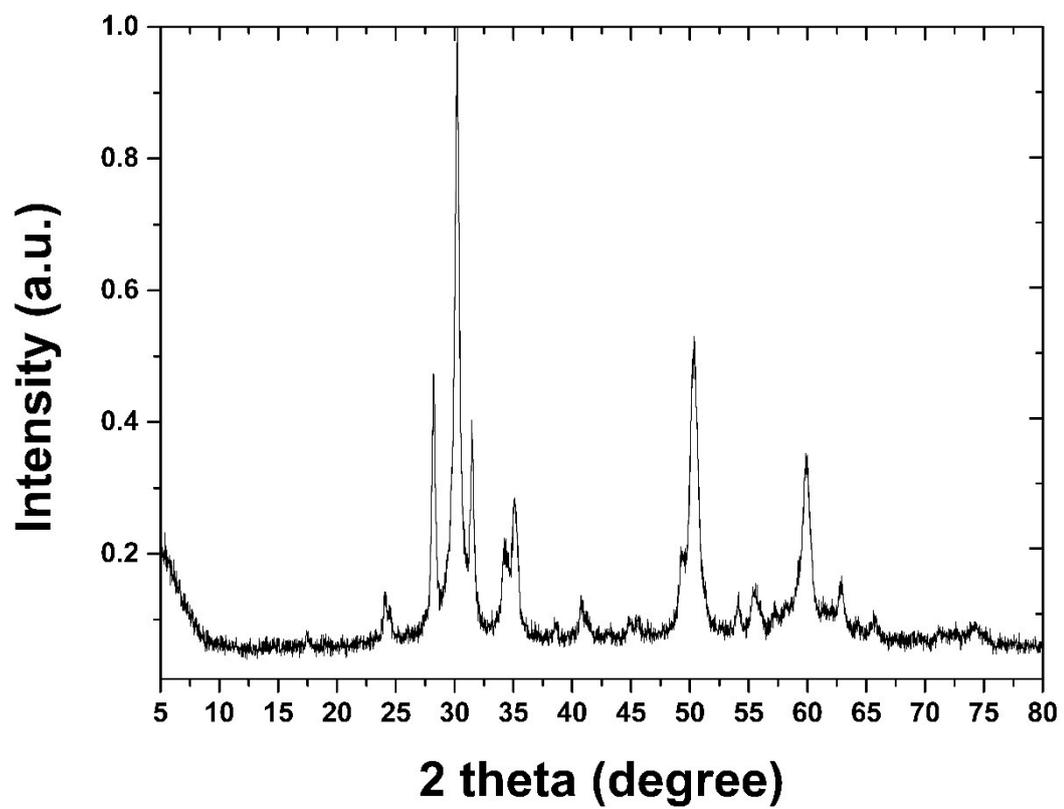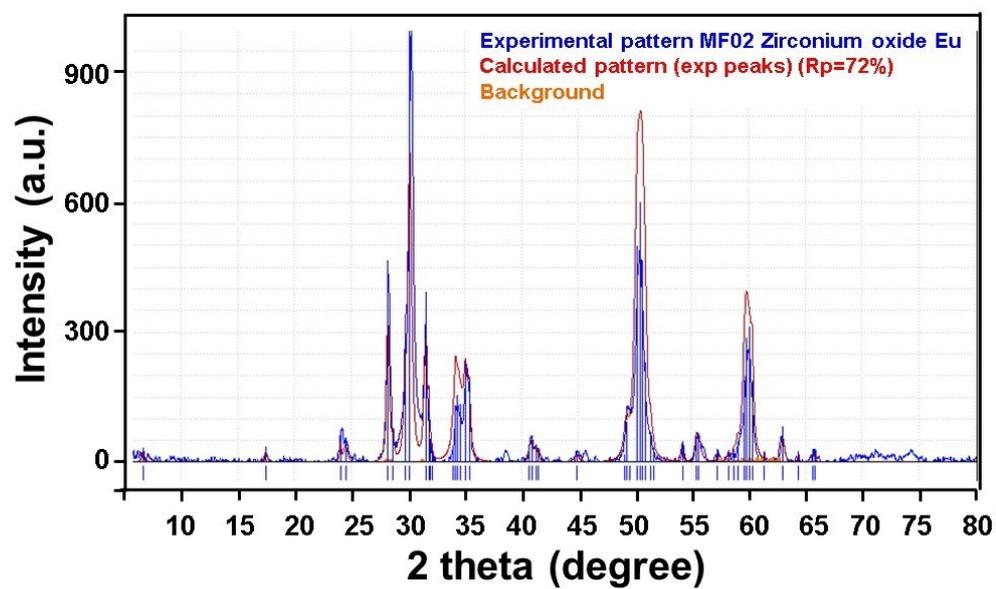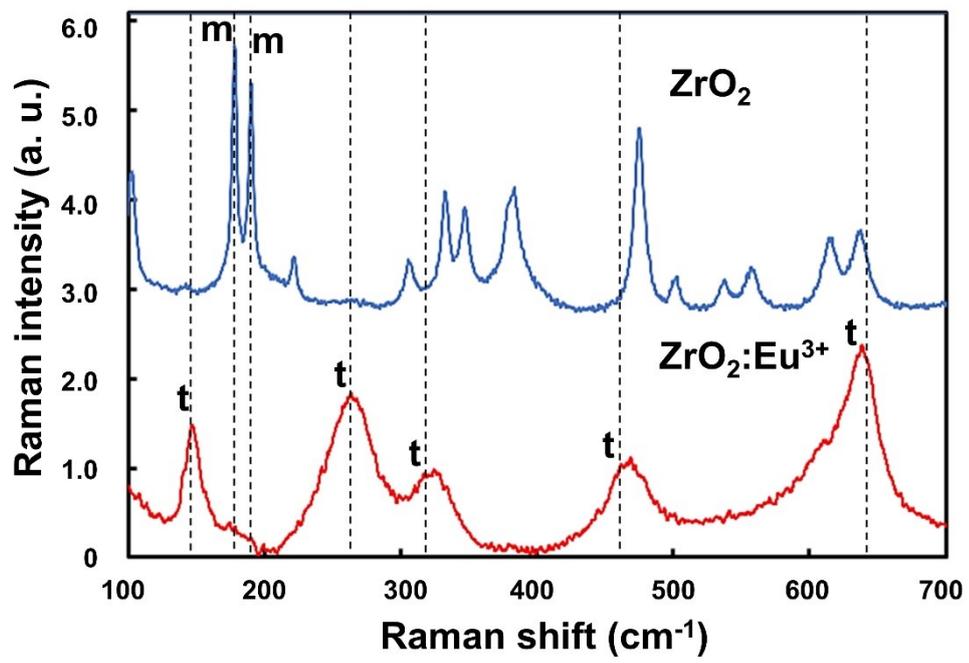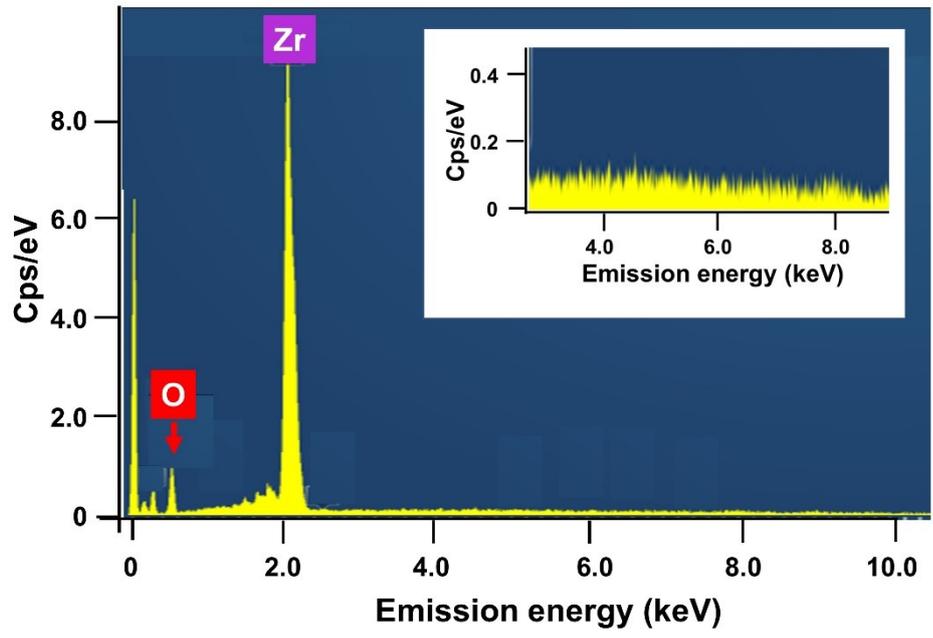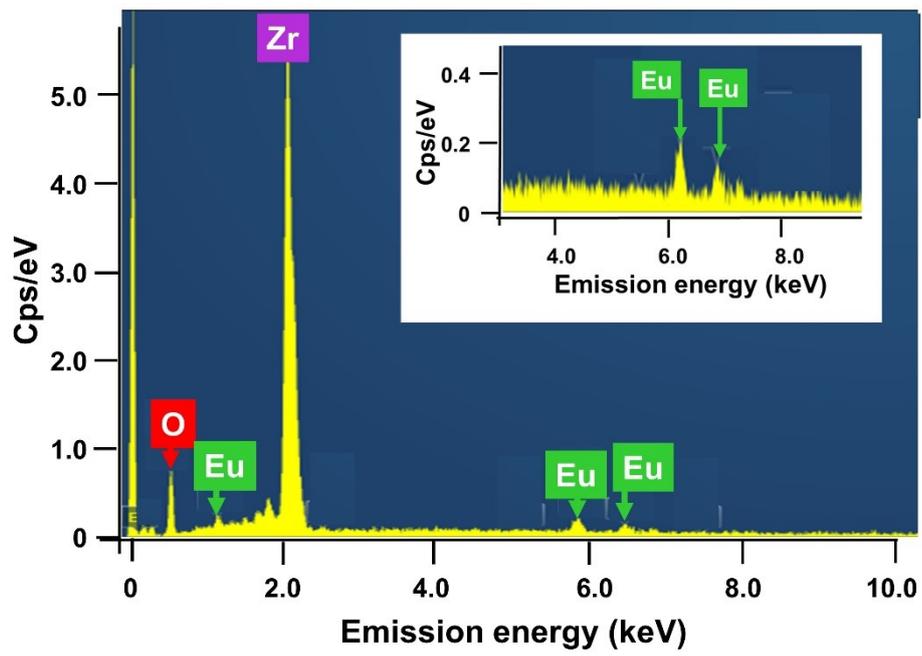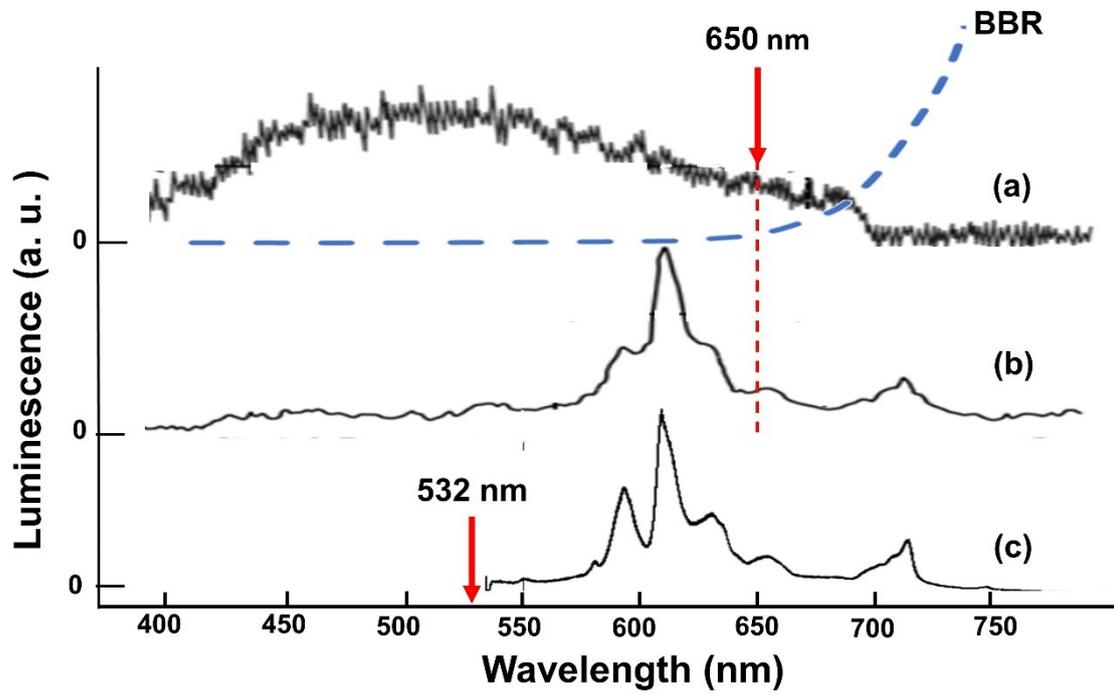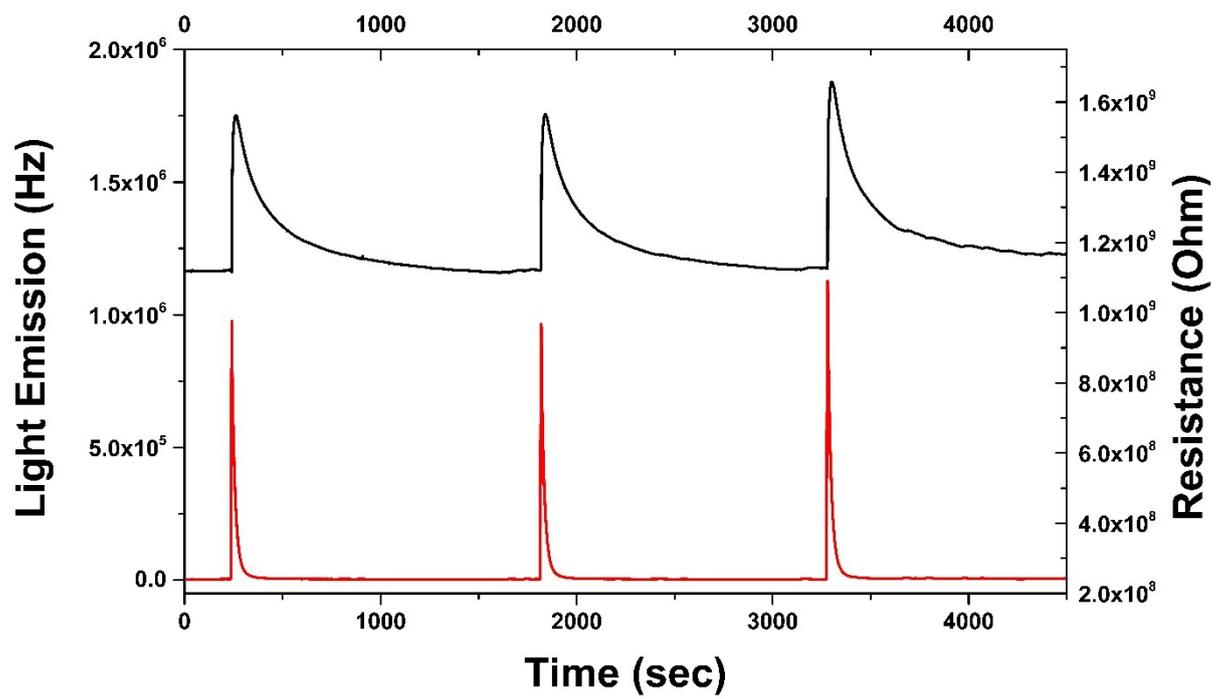
Supplementary Information

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690

691 **Rare Earth Doped Metal Oxide Sensor for the Multimodal Detection of Volatile**

692 **Organic Compounds (VOCs)**

693

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701 **S1. Heater characteristics**

702 The basic dimensions of the heater side of the sensor are reported in Table S1.

703 Additionally, the heater resistance at room temperature is of 10 Ohms A scheme of the

704 heater is reported in Figure S1. The heater resistance at room temperature is of 10

705 Ohms.

706 *Table 1: Basic dimensions of the heater side of the sensor*

Sensor feature	Dimensions	
		707
Heater track width	180µm	
		708
Gap between meanders	166µm	
		709
Contact pad width	1175µm	
		710
Contact pad length	500µm	
		711

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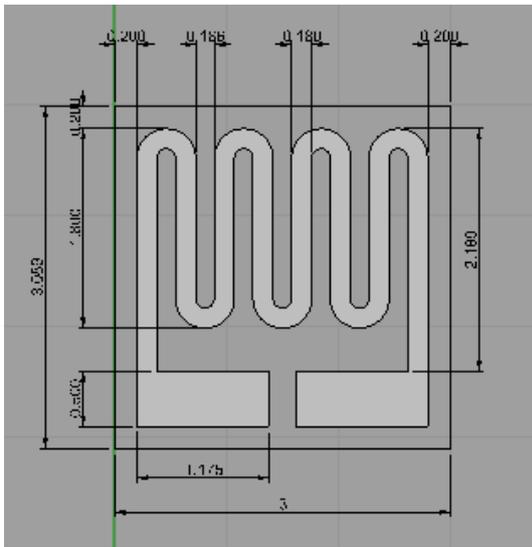
Figure 1 The heater employed during the eperiments

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S2. Dilution method validation: SIFT-MS

In the sensing experiments, different volatile concentrations were obtained using a 10 mL gas-tight syringe. To check the efficiency of the method, the concentrations reported in this paperwork were validated by selected ion flow tube (SIFT) mass spectrometry.

The SIFT-MS used for all the experiments is a Voice 200 (Syft technologies, New Zealand). The sample inlet was set to the default flow rate of 30 mL/min, with the inlet capillary and base both operating at 120°C. The dwell time for each mass was set to 1000ms or 100,000 counts depending on which was achieved first. Selected compounds for this method was acetone.

Different increasing dilutions were carried out by a 10 mL gas-tight glass syringe and injected into the machine. 1 mL of acetone headspace was taken from the vial. As a matter of example, a dilution of 1/10 was obtained by taking this 1 mL to 10 mL by the syringe and then coming back to 1 mL. Repeating the operation a second time allowed getting a concentration of 1/100, repeating three times of 1/1000 and so on. The 1 mL of the obtained concentration was then injected into the spectrometer. The results are reported as raw data in Figure S2.
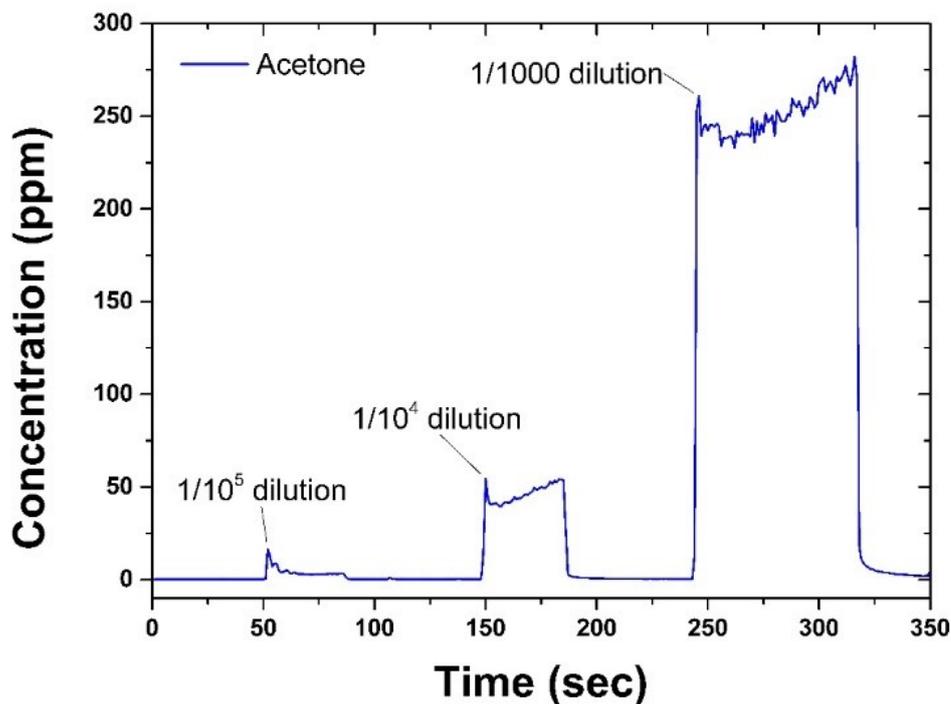
Figure S2. *Different levels of dilution, starting from the headspace concentration of acetone, registered by selected ion flow tube (SIFT) mass spectrometry.*

Also, it is possible to make a comparison between the expected values of acetone concentration expected by a given dilution, and the concentration effectively registered by the spectrometer. The slope obtained by linear regression of the SIFT-MS measured data vs the theoretical values of acetone concentration is reported in Figure S3. Four dilutions have ben taken into account, and the data registered by the SIFT-MS spectrometry are in good correlation with the theoretical values calculated.

The chart shows a plot with the equation:

$$y = 0.8252x + 17.655$$
$$R^2 = 0.9909$$

with x-axis labeled "Measured Concentration (ppm)" and y-axis labeled "Theoretical Concentration (ppm)".
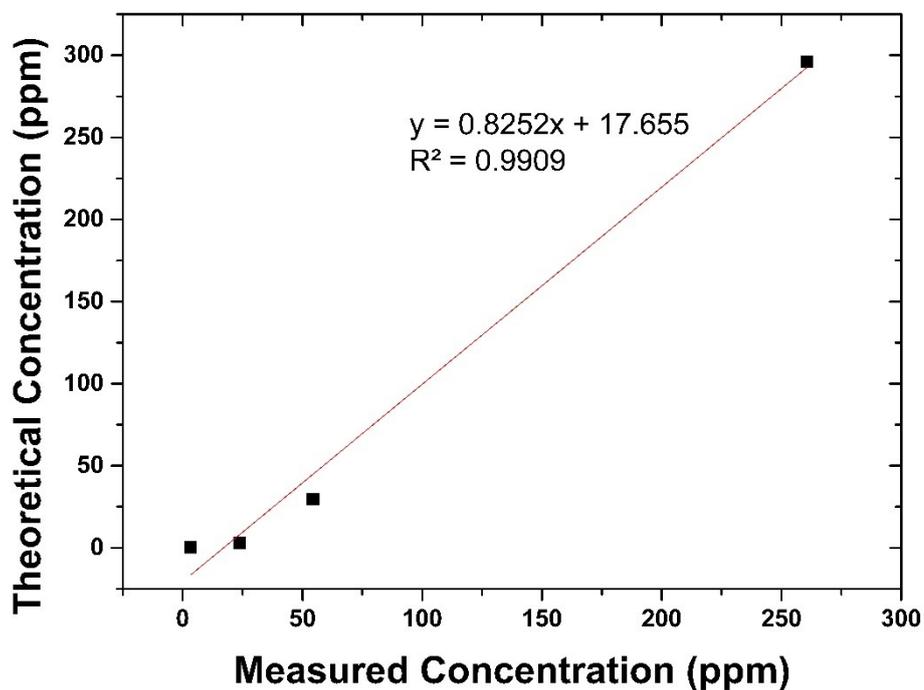
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750 *Figure S3 Theoretical acetone concentration as a function of the concentration measured by SIFT-MS*
751 *and carried out with the glass syringe-dilution method.*

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754

755 **S3. The sensor**

756 The typical sensor utilized during the study is reported in Figure S3, where it is possible

757 to observe the metal oxide nanopowder coating. In this case, a ZrO_2 nanopowder was

758 used.

759

760   *Figure S5 Sensor substrate drop-coated with ZrO_2 nanopowder.*

761