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Paper

An array of WO₃ and CTO heterojunction semiconducting metal oxide gas sensors used as a tool for explosive detection.

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Terrorists frequently use explosives and they represent an imminent threat to national and global security. Recent events highlight the necessity of explosive detection, demonstrating the need for developing and applying new sensors for explosive gas detection. Semiconducting metal oxide gas sensors can be incorporated into electronic noses, which provide a cheap, portable and highly sensitive device. Using unmodified, admixed and 2-layered sensors consisting of WO₃ and chromium titanium oxide (CTO), an array of seven heterojunction semiconducting metal oxide sensors was produced. All seven sensors were tested against four gases associated with explosive materials. The sensitivity was improved by using 2-layered sensors in response to ethanol, ammonia and nitromethane, whereas the admixed sensors showed high sensitivity when exposed to nitrogen dioxide. The selectivity of the array of sensors was tested using machine-learning techniques with a support vector machine. The technique produced good data classification when classifying the gases used within the study.

Introduction

Terrorism is a threat to public safety throughout the world, with its most common form using explosives to coerce and intimidate, which has taken the lives of more people than biological, chemical and radioactive threat substances combined[1]. With the increasing use of explosives by terrorist groups, detection of the hidden explosives within luggage, mail, vehicles, aircraft, or even on travellers is becoming a serious problem[2]. The widespread availability and accessibility of precursors, has led to terrorists using homemade explosives, rather than military or commercial explosives[3]. Therefore, making prevention and detection of explosives an increased challenge.

Many methods exist for the detection of explosives, such as magnetic metal detectors[4], X-ray[5] and thermal neutron analysis[6]. However, these techniques are currently lacking the sensitivity rates necessary for explosive detection[7]. Chemical detection of explosives, such as vapour detection, is therefore becoming the preferred method of explosive detection.

Metal oxide semiconducting (MOS) gas sensors are a reliable form of vapour detection[8], which have been found to be successful in detecting solvents associated with illicit drug manufacture[9]. The MOS sensors are small and easily produced, therefore making them a dependable method when gas sensing explosives[10]. MOS gas sensors are conductance-based sensors which function based upon the redox reactions occurring on the surface of the metal oxide when heated. The number of charge carriers on the metal oxide surface changes when in contact with test gases, which in turn alters the conductivity. MOS gas sensors are robust and inexpensive, however they currently lack the sensitivity and selectivity to detect low vapour pressure explosives.

Heterojunctions can increase semiconducting metal oxide sensitivity[11]. They are the combination of two different metal oxides admixed or layered together, which are essentially p–n, n-n and p-p diodes made from two pellets, a p and n type semiconductor[12]. Typically, the current is measured in the presence of gases by applying a forward bias voltage to the p–n contact[13]. The resistance of the sensing layer varies based on the recognition and transducer functions. If a single oxide is used within gas sensing these two functions cannot be optimised independently. Therefore, by introducing another metal oxide, which is sensitive to the test gas, both functions may be optimised simultaneously allowing the sensor to become more sensitive to gases at lower concentration[14]. P–n heterojunction systems have been studied for gas and humidity sensing, such as metal oxides SnO₂[15] and ZnO[16]. This technique shows promising results for potential enhancement of gas sensing properties when combined within an electronic nose.

Electronic noses, or e-noses, are defined as devices composed of an array of independently semi-selective and reversible gas sensors, such as conducting polymers [17,18]. Currently no single gas sensor is completely selective to a single chemical gas[19], therefore using a gas sensor array to detect different gases is a highly significant focus of research within gas sensing. The potential applications of the electronic nose are vast, such as explosive gas detection[20], use within the food industry[21] and pollutant gas detection within the environment[22]. Once the data is collected it can be processed with multivariate clustering techniques, such as support vector machines (SVM), where an algorithm, which treats the data as a series of binary class problems, separates multiclass data. A SVM will be used within this study to classify the multiclass data collected from the test gas exposed sensors, in order to establish a unique gas fingerprint and

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allow the different test gases to be easily distinguished and thus improve selectivity.

Here we investigate the use of semiconducting metal oxide gas sensors as a tool to detect a range of gases associated with explosives. In order to investigate sensitivity and selectivity of metal oxides, an array of unmodified, admixed and 2-layered sensors of WO_3 and chromium titanium oxide (CTO) were produced. The metal oxides were selected on the basis of their efficacy in detecting NO_2 and NO in cases for WO_3[23], and ethanol in cases of CTO[24]. All sensors produced were tested against four gases associated with explosives, nitrogen dioxide, ammonia, ethanol and nitromethane.

The materials used within military propellants and explosives are mostly organic compounds containing nitro (NO_2) groups[25]. Consequently, the sensor responses to NO_2 for explosive detection are highly significant. Ethanol is a colourless, volatile liquid used within the production of explosives, and therefore is an important gas to be sensed[26]. Ammonia is a colourless gas with a pungent odour, which is extensively used within the production of explosives[27], fertilizers[28], and as an industrial coolant[29]. Ammonia is a reducing gas and a potential indicator of homemade explosives[30]. Nitromethane is regularly used within motor sport[1] and thus as a readily acquired liquid, it has also been used within the preparation of homemade explosives[31]. Nitromethane is more energetically explosive than TNT; therefore, the detection of nitromethane within gas sensing is essential[1]. There is limited research currently being conducted on the MOS gas sensing of $MeNO_2$.

The data collected were processed against a support vector machine in order to comprehend the sensors application into an electronic nose. This is the first instance, to our knowledge, of admixing of CTO and WO_3 for gas sensing purposes. The abbreviations used within the study can be seen within table 1.

Experimental

The synthesis of CTO, with target stoichiometry $Cr_{1.65}Ti_{0.35}O_3$, was carried out by ball milling stoichiometric amounts of TiO_2 powder (Sigma Aldrich) and Cr_2O_3 powder (Sentury Reagents, 99.9%) in 32 mL of Iso-Propyl-Alcohol (IPA) (Emplura, Merck). The mixture of metal oxides, together with 6 mm alumina grinding balls, were ball milled in a Nannetti Speedy 1 ball-milling machine for 5 minutes. This process was repeated three times in order to produce a viscous mixture. Once the solvent had evaporated, the powder was placed within a furnace (Elite Thermal Systems Limited) for 5 hours in order to dry the powder and to establish the evaporation of IPA.

An agate pestle and mortar was used to grind the dried powder, which was thereafter sieved through a 150 μm sieve. In order for the final product to form, the powder was then placed into the furnace at 900°C for 12 hours. The sensors were produced by firstly mixing the selected metal oxide(s) with an organic vehicle ESL-400 (Agmet, Ltd), in a pestle and mortar for 20 minutes to create a homogenous ink. The metal oxide paste was then screen-printed onto the gold interdigitated patterned electrodes on the 3 mm by 3 mm alumina substrates (Dynamic microcircuits) using a DEK 1202 screen-printer. When screen-printed the ink was allowed to dry under an infrared lamp for approximately 10 minutes. Once dry the substrates were allowed to cool prior to subsequent layers being printed. The alumina substrates were layered four times with the appropriate metal oxide using this method.

After screen-printing, the individual sensor chips were placed in the Elite thermal systems BRF14/5-2416-2116 furnace for an hour at 600°C, allowing the organic vehicle to be burnt off and to strengthen the metal oxide film to fully bind to the gold electrodes. Using a Macgregor DC601 parallel gap resistance welder, platinum wire, (Alfa Aesar, 0.0508 mm diameter and 99.95% metals basis), was spot-welded onto the gold contacts at the end of the platinum heater track on the base of the substrate and the gold electrode contacts on the top of the substrate. Following this the substrates were welded onto the metal pins of the sensor housings, from which the sensor could be suspended, therefore allowing the sensor to be placed into the rig. Once welded the completed sensors were then exposed to a 1000 cm^3 min^{-1} flow of dry air (BOC) at 500°C for 2 hours on the rig to remove any residual gases.

All gas-sensing experiments were carried out using an in-house testing rig, located within UCL. The rig was comprised of 12 glass chamber ports, which connected to the gas supplies. The sensor resistance measurements were collected through the use of potential divider circuits, coupled to an analogue-to-digital converter and a PC. The gas flow through to the sensor chambers was regulated by Tylan Gerneral Mass Flow Controllers (MFC's) (model FC-260) and Bürkert 2/2-way Solenoid Valves (SV's) (model 0124). A Wheatstone bridge circuit and a platinum heater track found on the back of each sensor produced were used to accomplish sensor heating. The sensors were exposed to four test gases associated with explosives at temperatures 300°C, 400°C and 500°C. The concentration of the gases used were 10, 20, 40, 80, 100% of their source concentration, which were 100 ppm for ethanol, 50 ppm for ammonia and 7200 ppm for nitromethane. However, the concentration of nitrogen dioxide used was 5, 10, 20, 40 and 50% of its source concentration at 200 ppm. Before any exposure to the test gases, all sensors were exposed to dry air for 30 minutes, allowing the baseline resistance to be established. Pulse lengths of the test gases were set to 600 seconds in order to gain a maximum response.

Sensor Abbreviation	Metal Oxide (4 layers)
WO_3	WO_3 (100%)
CTO	Chromium titanium oxide (100%)
2L WO_3	2 layers of WO_3 over 2 layers of CTO
2L CTO	2 layers of CTO over 2 layers of WO_3
75% WO_3	75% WO_3, 25% CTO
75% CTO	75% CTO, 25% WO_3
50/50	50% CTO, 50% WO_3

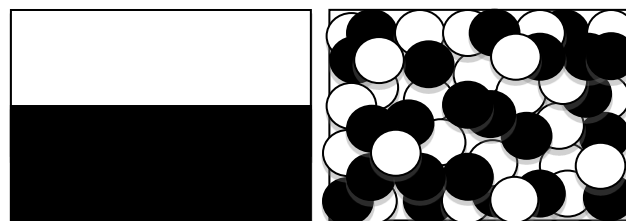Table 1. The abbreviations used within the study

Figure 1. The morphology of a 2-layered sensor (left) showing 2 layers of one metal oxide layered on top of another 2 layers of another metal oxide. A 50/50 admixed sensor (right) is shown where the metal oxides are admixed before being screen-printed.

Between each test gas pulse 2000 seconds of dry air was exposed to the sensors, to allow the sensors to regain their baseline resistance. Once a test gas exposure was completed, dry air was exposed to the sensors for 2 hours, in order to remove any test gas from the sensor chamber, therefore allowing no contamination for the subsequent test gas exposures. In order to show repeatability at least 2 repeat measurements were carried out.

Results and Discussion

Characterisation

The syntheses of seven semiconducting metal oxides, specifically chosen based on their sensitivity to gases associated with explosives, were produced using a thick film screen-printing technique. All seven sensors were exposed to four gases and to temperatures, 300°C, 400°C and 500°C. All sensors produced underwent several characterisation techniques, both before and after being exposed to the test gases, including Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Energy-Dispersive X-ray Spectroscopy (EDX) and Raman spectroscopy.

The micrographs produced using the Hitachi S-3400N microscope with a 20 kV SEM probe show the porous nature of the metal oxide sensors both unmodified and admixed. All sensors show spherical particles ranging in size. The measurements of the particles were taken from the x2000 zoom using a length measuring tool within the Hitachi S3400N software. The unmodified WO_3 showed the larger particles with an average size of 9.4 μm. The unmodified CTO particle size on average was 7.7 μm. Figure 2 shows the micrographs produced for unmodified WO_3 and CTO sensors.

The EDX analysis was preformed to determine the composition of the array of sensors. The weight percentages produced from the EDX with 20 kV SEM probe coupled with Oxford Instruments' INCA X-Sight system for each sensor before exposure to test gases, showed the resulting atom types for all sensors as expected. The weight percentages of the sensors can be seen within table 2.

The Brucker GADDS D8 diffractometer XRD with 2θ range 21° to 64°, produced diffraction patterns of the array before analysis can be seen within figure 3, which confirm the chemical make-up of the unmodified metal oxides, the 2-layered and admixed sensors. The unmodified CTO eskoalite structure had strong peaks at 2θ = 24.5°, 34°, 36.0°, 42° and 55°, which has been identified by observation as $CrTiO_3$ within the Joint Committee on Powder Diffraction Standards
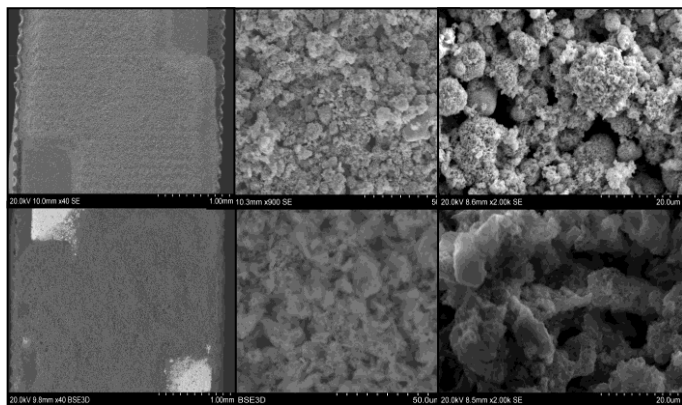
Sensor	O	W	Cr	Ti	Total
WO₃	21	79	-	-	100
CTO	34	-	55	11	100
2L WO₃	21	79	-	-	100
2L CTO	34	-	56	10	100
75% WO₃	25	52	19	4	100
75% CTO	30	21	41	8	100
50/50	26	42	28	4	100

Table 2. EDX weight percentages produced from the array of sensors.

(JCPDS pattern 33-408). WO_3 displays a monoclinic system, with characteristic peaks at 2θ = 23.1°, 23.6°, 24.4° and 34.2°, which are apparent in all WO_3 containing samples. The WO_3 monoclinic structure can be matched with the JCPDS (number: 71-1465). The 2-layered CTO sensor (2 layers of CTO over 2 layers of WO_3) shows WO_3 peaks, as tungsten is a larger atom than either titanium or chromium and thus scatters the X-rays much more strongly, whereas no titanium or chromium can be seen within the 2L WO_3 sensor (2 layers of WO_3 over 2 layers of CTO).

Raman spectroscopy was performed using a Renshaw inVia Raman Microscope using 514 nm laser and wavenumbers ranging from 200 cm⁻¹ to 2000 cm⁻¹; above 1000 cm⁻¹ there were no noticeable peaks. The major vibrational modes seen within the WO_3 containing samples were 270 cm⁻¹ (a), 718 cm⁻¹ (b) and 808 cm⁻¹ (c). These modes correlate to the stretching of O-W-O, the stretching of O-W and the bending of O-W-O respectively, and thus confirm the
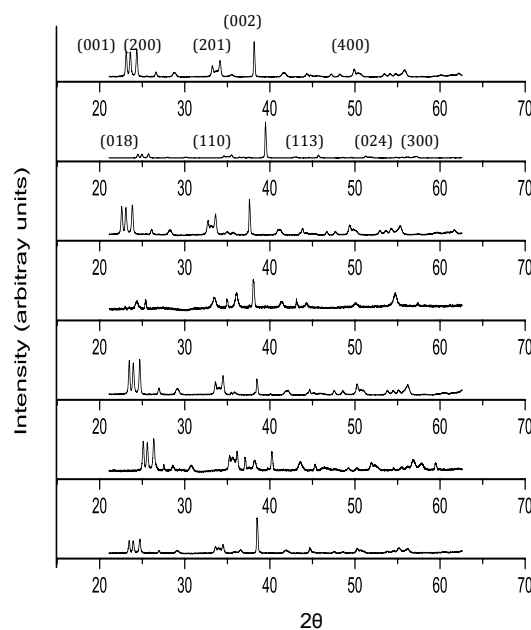

Figure 2. SEM micrographs of unmodified WO_3 (top) and CTO (bottom) at magnifications x40, x900 and x2000.

Figure 3. XRD diffraction patterns of an array of seven sensors, (top) WO_3, CTO, 2L WO_3, 2L CTO, 75% WO_3 75% CTO, and 50/50.
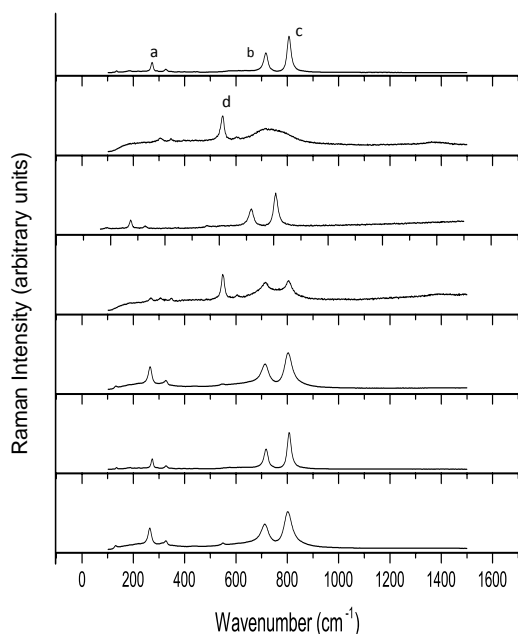
Figure 4. Raman spectra of an array of seven sensors (top) WO_3, CTO, 2L WO_3, 2L CTO, 75% WO_3, 75% CTO and 50/50.

compound as monoclinic tungsten trioxide[32,33]. However, the unmodified CTO sensor produced its dominant peak at 550 cm^{-1} (d), which is characteristic of crystalline α-Cr_2O_3[34,35]. All characterisations were repeated after exposure to the tests gases and high temperatures. No changes within the structure of the metal oxides were detected.

Gas Sensing Results

The sensitivity of the sensor was calculated by comparing the baseline resistance of the sensor when within air (R_0) and the resistance when exposed to the test gas (R). The response magnitude for an n-type material when exposed to an oxidising gas creates an increase in resistance, otherwise known as a resistive response R/R_0, whereas when exposed to a reducing gas, a decrease in resistance and thus a conductive response R_0/R would be produced. For a p-type material the opposite effect can be seen. Both resistive and conductive responses were seen within the results. The magnitude of response, S, was calculated as $S = R_{max} - R_0$ for the gas pulses of NO_2, NH_3, EtOH and $MeNO_2$, where R_{max} was the maximum sensitivity produced. As established within the study the magnitude of response increases with analyte concentration. This process can be seen within figure 5, where the admixed sensors showed greater sensitivity to 10, 20, 40, 80 and 100 ppm of nitrogen dioxide at 300°C than the 2-layered sensors. The sensitivity of the sensors generally decreased with operating temperature. However, ammonia gas produced its most sensitive results at the highest temperature.

The conductivity of the metal oxide is altered due to the interactions between temperature dependent absorbed oxygen species on the surface of the metal oxide, which produce a depletion region. This interaction changes the resistivity of the metal oxide, as the conductivity of the material is dependent on the size of the depletion region. Hence when within air an increase in conduction is seen and a baseline resistance established (eqn 1).
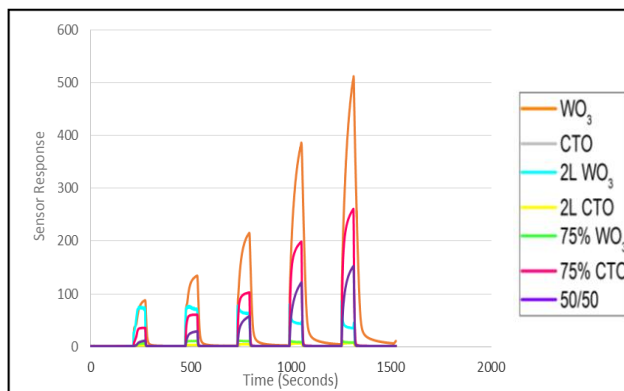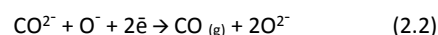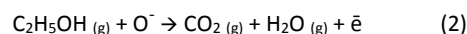
$$O_{2 (g)} + 2\bar{e} \rightarrow 2O^- \qquad (1)$$

Figure 5. An array of sensors tested with NO_2 at concentrations 10, 20, 40, 80 and 100 ppm at 300°C.

Results on the reducing gases

An n-type semiconductor when exposed with a reducing gas, such as ethanol, creates an oxidation reaction with the oxygen species on the surface of the oxide, which in turn form CO_2 molecules. The CO_2 molecules disperse from the metal oxide and electrons are released into the depletion layer, producing a decrease in resistivity (eqn 2).

$$C_2H_5OH_{(g)} + O^- \rightarrow CO_{2 (g)} + H_2O_{(g)} + \bar{e} \qquad (2)$$

$$CO_{2 (g)} + \bar{e} \rightarrow CO^{2-} \qquad (2.1)$$

$$CO^{2-} + O^- + 2\bar{e} \rightarrow CO_{(g)} + 2O^{2-} \qquad (2.2)$$

Oxygen species are formed on the surface of the p-type metal oxide, which in turn forms a hole accumulation layer (HAL). Therefore, when a reducing gas, such as ethanol, is exposed to a p-type material it interacts with the oxygen species, which release electrons into the metal oxide. The electrons consequently interact with the positive holes within the HAL, thus increasing the resistance.

The response produced from the unmodified tungsten trioxide sensor when tested against ethanol is considerably lower than those reported in previous literature[36,37]. The reaction pathway shown within eqn 2 could explain the low response produced with the unmodified WO_3 sensor of R/R_0 1.75, when exposed to ethanol at 10,
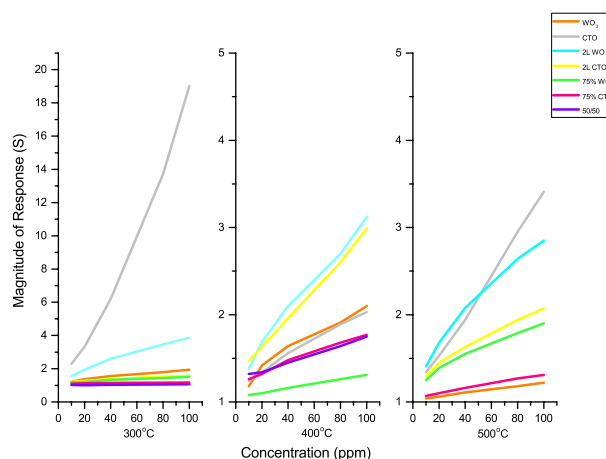

Figure 6. The magnitude of response for an array of sensors exposed to EtOH at 300°C, 400°C and 500°C.
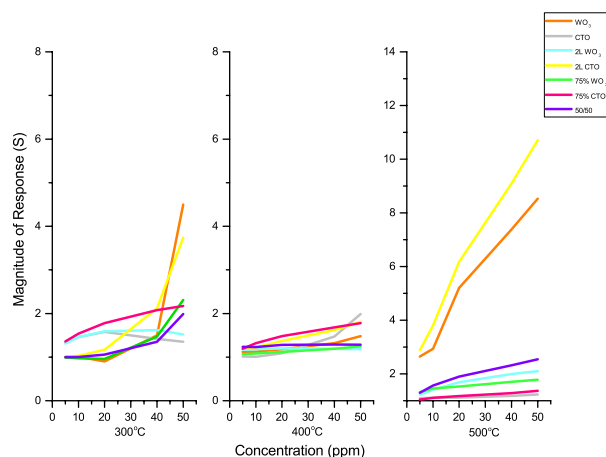
Figure 7. The magnitude of response for an array of sensors exposed to NH_3 at 300°C, 400°C and 500°C.

20, 40, 80 and 100 ppm. WO_3 has previously shown low sensitivity when exposed to CO and thus this reaction may in turn reduce the sensitivity[38] (eqn 2.2). As seen within figure 6, at 300°C unmodified CTO produced the highest sensitivity of 19 R/R_0, whereas at 400°C both the 2-layered sensors exhibited the highest sensitivity at 3 R/R_0, therefore showing CTO as being selective towards ethanol compared to the remaining sensors within the array. Although less research is available on the gas sensing properties of CTO, previous research concludes equivalent responses produced with an unmodified CTO sensor exposed to ethanol at the same temperatures and concentrations[39].

Within the ammonia testing, the highest sensitivity could be seen at 500°C for unmodified WO_3 and 2L CTO (2 layers of CTO over 2 layers of WO_3) at R_0/R 8.5 and R/R_0 10.7 respectively. All sensors were exposed to concentrations 5, 10, 20, 40 and 50 ppm of ammonia. This result proved surprising as unmodified CTO produced one of the lowest resistive responses, showing 2-layered sensors to increase sensitivity. Previous research on gas sensing in advance of 100 ppm of ammonia using tungsten trioxide has produced low responses of 2.5 R_0/R when carried out at 300°C[40]. As seen within figure 7, the study conducted produced an increased conductive response of the unmodified WO_3 to 50 ppm of ammonia at R_0/R at 300°C, with the 2L CTO sensor (2layers of CTO over 2 layers of WO_3) producing a resistive response of 3.8 R/R_0. Therefore, the sensitivity
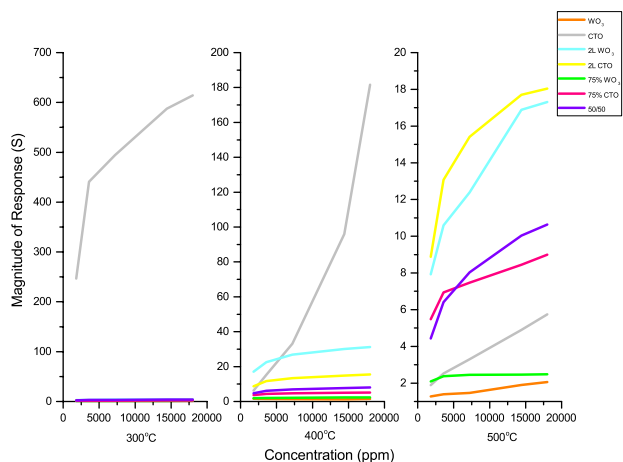
has significantly improved using the array of sensors when tested against ammonia.

A fall in resistance could be seen when exposed to the reducing test gases due to the oxidation of oxygen species on the surface of the sensor. The CTO containing sensors produced the highest resistive response, as seen within figure 8, with unmodified CTO producing an R/R_0 of 167 when tested at 300°C. Consequently, showing the unmodified CTO as being highly sensitive when tested against nitromethane. Literature on the gas sensing properties of nitromethane are limited, therefore these results prove promising for establishing the successful responses produced when exposed to a p-type material.

Results on the oxidising gas

The array of sensors was exposed to five concentrations ranging between 10 and 100 ppm of nitrogen dioxide. Exposing an oxidising in resistance, and thus a resistive response (R/R_0), as electrons leave the metal oxide surface. The outcome produces a decrease in the charge carrier concentration results and an increase within the depletion layer (eqn 3).

$$NO_{2\,(g)} + \bar{e} \rightarrow NO_2^- \qquad (3)$$
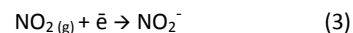
The sensors sensitivity gradually increased with gas concentration and decreasing temperature, accordingly displaying maximum responses at 300°C, as seen within figure 9. Tungsten trioxide produced an extremely high resistive response of 512 R/R_0, when exposed to NO_2. Previous studies have shown a resistive response of WO_3 to 100 ppm NO_2 at 200 R/R_0[41], where a resistive response of 215 R/R_0 at 40 ppm of NO_2 can be seen within this study; therefore, establishing an increase within sensitivity.

As seen within the results, when exposed to an oxidising gas the p-type metal oxide surface rapidly decreases its concentration of electrons, consequently decreasing the metal oxides resistivity and producing a conductive response. Conversely, all CTO based sensors produced a conductive response significantly lower than unmodified WO_3. However, the CTO modified sensors showed a substantial response when compared to the unmodified CTO sensor. A conductive response of 261 R_0/R was produced by 75% CTO (75% CTO and 25% WO_3) which is 37.2-fold increase than the unmodified CTO. The 50/50 (50% CTO and 50% WO_3) sensor also produced an elevated conductive response of R_0/R 152, indicating that the doping of p-type CTO with n-type WO_3 can successfully increase sensitivity against gases associated with explosives. The admixed sensors

Figure 8. The magnitude of response for an array of sensors exposed to $MeNO_2$ at 300°C, 400°C and 500°C.
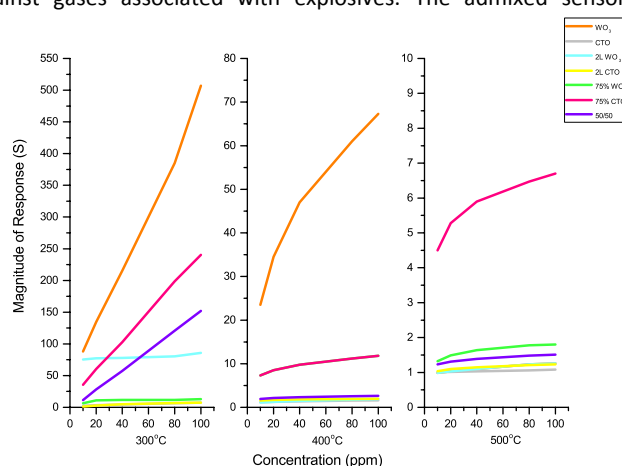

Figure 9. The magnitude of response for an array of sensors exposed to NO_2 at 300°C, 400°C and 500°C.

demonstrated a significant improvement within sensitivity when tested against NO_2 and when compared against the 2-layered sensors. The highest of the 2-layered sensors 2L WO_3 (2 layers of WO_3 over 2 layers of CTO) produced a resistive response of 86 R/R_0.

Overview of gas sensing results

Overall, the highest sensitivity for an oxidising gas was unmodified WO_3, and the three admixture sensors, 75% CTO (75% CTO and 25% WO_3), 50/50 (50% CTO and 50% WO_3) and 75% WO_3 (75% WO_3 and 25% CTO) suggesting n-type semiconductors to be more sensitive towards NO_2. Previous research has yielded evidence of admixed sensors producing more sensitive results than the unmodified metal oxides[42]. WO_3 has been investigated and used within metal oxide admixtures and has produced a higher sensitivity than its unmodified version[43]. Suchorska-Woźniak et al, states WO_3 has been previously used within a hetero-contact gas sensor, which modified the parameters of the sensor and thus increased its sensitivity[44]. It is thought that the admixed sensors improve sensitivity due to the change within pore structure as seen from the SEM results. 75% CTO (75% CTO and 25% WO_3) produced a response of 261 R_0/R, this potentially may be due to CTO having a smaller range of pore size compared to WO_3 and thus may create a larger surface area when admixed. Therefore, further investigation of WO_3 within a hetero-junction, in particularly admixed with a p-type material, should be conducted.

The highest sensitive sensors for a reducing gas were unmodified CTO, 2L CTO, (2 layers of CTO over 2 layers of WO_3), 2L WO_3 (2 layers of WO_3 over 2 layers of CTO) and 75% CTO (75% CTO and 25% WO_3). Therefore, it is clear that CTO containing sensors produces a high response against all three reducing gases. However, within the ammonia testing unmodified WO_3 also produced a sensitive result of 8.5 R_0/R at 50 ppm, whereas Stivastava et al, found a poor sensitivity response of 1 R_0/R produced when sensing WO_3 to 1000 ppm of ammonia[45].

Both 2-layered sensors also provided high responses when exposed to the reducing gases, such as 2L CTO (2 layers of CTO over 2 layers of WO_3) producing a R/R_0 value of 21 when exposed to nitromethane at 400°C. Research has shown 2-layered sensors, such as WO_3 and SnO_2 to produce high sensitivities when exposed to hydrogen sulphide[46]. Multiple layers of different metal oxides hetero-junctions have been investigated, although 2-layered semiconducting gas sensors may improve sensitivity, it may also decrease it[47], as seen within the gas sensing of nitromethane and ethanol. However, 2-layered sensors can be characterised by producing better selectivity when exposed to the test gases.

The characterisation techniques used within the study, validate

Classification				
Class	**NO_2**	**NH_3**	**EtOH**	**$MeNO_2$**
NO_2	58	4	14	0
NH_3	16	23	39	0
EtOH	5	6	58	0
$MeNO_2$	0	0	0	71

Table 3. Confusion matrix for the SMO, True class is defined vertically with the output classification horizontally, classification accuracy was 71.4%.

that the gas sensors are able to retain their structures and thus not be physically changed due to gas exposure or calcination, after over 40 experimental cycles, therefore suggesting long term microstructural stability. The response values produced also remained consistent throughout the 40 experimental cycles, consequently also signifying response stability. Each experiment was conducted a minimum of three times, in order to investigate the consistency of the array. Given the experiments produced little variation between each experiment, the authors suggest the array of sensors to be reliable in producing a dependable technique for gas sensing. The array is easily reproducible through the screen-printing method, with a low cost associated with the production.

Results of the Support Vector Machines

A support vector machine training algorithm was used within this study to build a model to classify the data produced from the gases tested. This model aims to demonstrate the selectivity of the sensors if implemented into an electronic nose. The data obtained was analysed in order to classify nitrogen dioxide, ethanol, ammonia and nitromethane when tested against the heterojunction array of sensors. Performed on WEKA and designed by Platt, the tool used was sequential minimal optimization (SMO), which applied a one against one technique to separate the multiple classes of data[48, 49]. The cost and Kernel parameters were adjusted in order to refine the values.

A data set of 840 vectors was produced, containing an array of seven sensors tested against four test gases over a range of temperatures. The data set used included the maximum responses found within each gas pulse at given concentrations for exposure to 600 seconds gas pulses of NO_2, NH_3, EtOH and $MeNO_2$. Also included was the first 50 seconds of conductive and resistive responses produced, therefore showing the change in resistivity was also included within the data set. The final variable included was data on the sensor temperature. The optimum results were found when the parameters were increased, operating the cost parameter at 6000 and with a percentage split of 65%. The algorithm produced 71.4% accuracy for classification of the gases, which describes the models ability to identify the test gases based upon the resistive and conductive responses produced within the data set implemented. As seen within table 3, NO_2 was readily identified due to its oxidising response and $MeNO_2$ due to its concentration. However, as NH_3 and EtOH are both reducing gases they proved to be the most confused and thus produced similar results.

A high level of selectivity can be achieved using an array of sensors, combined with machine learning techniques such as SMO. Currently no single sensor produces absolute selectivity; nevertheless, the results produced within this study have shown a high level of selectivity to a variety of associated explosive gases. Overall WO_3 and CTO unmodified, admixed and 2-layered sensors produced a good sensitive array of sensors with potential to be incorporated within an electronic nose system for the detection of explosive vapours.

Conclusion

Seven sensors were produced, characterised and tested against the chosen gases. The results produced show MOS sensors are capable of detecting gases associated with explosives. A heterojunction array of gas sensors has not previously been used for the detection of gases associated with explosives. Heterojunction arrays used for gas sensing properties have previously been researched, however the

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combination of an n-type and a p-type are far less well-known. The array produced within this study has to the authors knowledge, never been published before, therefore demonstrating its novelty by conducting an experiment aimed at the detection of gases associated with explosives, through the use of a heterojunction array of gas sensors.

Generally, admixtures of n-type and p-type semiconductors have increased responses to be oxidising and reducing gases. Whereas the 2-layered sensors produced, proved highly successful when detecting ethanol. Currently a single sensor does not have the selectivity required for the detection of explosives, however using an array of the seven sensors produced and tested here has shown selectivity between ranges of associated explosive vapours. It is suggested that potentially further increase of selectivity within MOS sensors to test gases could be achieved through the use of hetero-junctions. Both admixtures of metal oxides and 2-layered metal oxides have been shown to enhance sensor response.

All classification tests of the sensors after being exposed to the test gases and high temperatures showed no structural change to the materials indicating that the unmodified, 2-layered and admixed WO$_3$ and CTO sensors would present strong repeatability and reproducibility.

The results produced are very encouraging and thus further study should be commenced on hetero-junctions used within gas sensing. A portable device produced in order to reduce the number of explosives using this technology could be achieved, due to the improving sensitivity to associated explosive gases, the ease of the production of the sensors and the low cost of the electronics required.

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