



Properties of Purified and Platinum Decorated Chemical Vapor Deposition Grown Multi Walled Carbon Nanotubes

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ABSTRACT

Multi walled carbon nanotubes (MWCNTs) are known to respond well to a range of gases and vapors. Metallic additives are often introduced to improve the sensitivity and selectivity to some gases. Here the difference in response between MWCNT sensors with and without a metal additive is discussed for a range of gases. Resistive sensors fabricated from chemical vapor deposition (CVD) grown multi walled carbon nanotubes (MWCNTs) collected between gold microelectrodes by dielectrophoresis are presented as a cheap, saleable and facile method of producing carbon nanotube gas sensors. The MWCNTs sensors were exposed to a series of test gases including NO₂, NH₃, CO and H₂ and exhibited low ppm. Increasing the temperature not only reduced the recovery time of the sensors, but also increased the sensitivity to some gases whilst a decrease in the sensitivity was seen for other gases. A method for decorating MWCNTs with nanometer sized Pt particles is presented and compared as a sensing material to purified MWCNTs which have undergone acid reflux and base washing. The role of defects and the sensing mechanisms are discussed.

1. Introduction

CNT sensors show response for ppm levels of a range of gases at room temperature, making them ideal for low temperature applications or applications where low power consumption is required. While at low temperatures recovery times are long for many gases, running the sensors at temperatures above room temperature reduces the recovery time significantly.

Temperature affects not only the recovery time but also the sensitivity and selectivity of the MWCNT sensors. It is demonstrated that higher temperatures can enhance or decrease the response of a MWCNT sensor to a gas. For gases which only weakly physisorb to the MWCNTs lower temperatures are required for maximum sensitivity, as at higher temperatures this mechanism becomes unfavorable. Processing and purification of CNTs also has an effect on the gas sensitivity of MWCNT sensors as the tube walls can be modified with acid groups during the process, and defects in the tube walls may be increased. Modifications such as the decoration of the MWCNTs with metal nanoparticles, also affect the dominant sensing mechanism. The mechanisms of sensing are elucidated by comparison of the magnitude of response of modified MWCNTs at different temperatures [12].

2. Experimental

2.1. Synthesis of Carbon Nanotubes

The CVD equipment used is similar to that described by Andrews et al. [1]. The growth parameters were varied until long aligned mats of MWCNTs were grown. The growth parameters used are based on those described by Singh et al. [15]. A brief

description of both CVD apparatus and growth parameters follows. A solution of 3wt% ferrocene in toluene was injected into a two-stage tube furnace using a motorised syringe pump. The first stage of the furnace was maintained at 200°C where the solution vaporizes. The mixture then flows into the main tube furnace which is maintained at 760°C by a temperature controller.

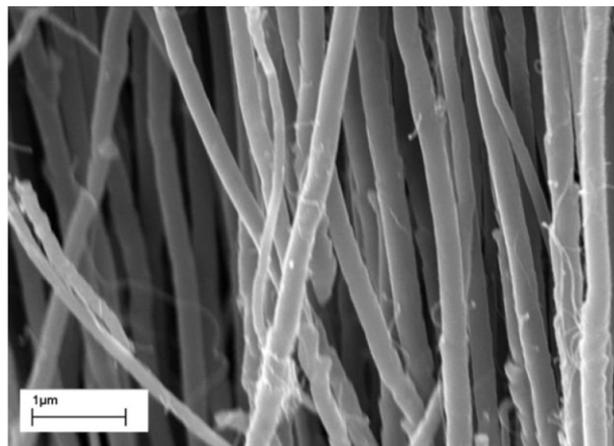


Fig. 1 SEM image showing a mat of long, entangled and aligned MWCNTs

The growth substrate was a quartz tube with internal diameter of 46 mm. A mixture of argon and 10% hydrogen was used as the carrier gas. The total gas flow rate was maintained at 2000 ml/min, and the injection rate of ferrocene in toluene was 5 ml/hour. The ferrocene decomposes to provide the iron catalyst required to nucleate the CNT growth with an Fe particle found at the root of each CNT, whereas toluene acts as the carbon feedstock. Figure 1 shows an SEM image of these MWCNTs which in long (500 μm), entangled, aligned mats perpendicular to the walls of the quartz furnace tube.

2.2. Purification and Modification of Carbon Nanotubes

Acid refluxes are commonly used to improve the

purity and dispersibility of CNTs in aqueous solution. It has recently been shown [17] that including a base washing step after the acid reflux removes residual impurities and contaminants associated with this process. Figures 2a and 2b show the CNTs before and after purification respectively.

The purification process which has been used in this work has been discussed elsewhere [17], however a brief description will be given. The acid reflux continued as has frequently been described in the literature [6]; MWCNTs grown by CVD were refluxed in a 3:1 concentrated H₂SO₄/HNO₃ mixture at 120°C for 30 min, and then thoroughly washed with distilled water, until the filtrate was colourless and pH neutral. The refluxed CNTs formed a stable dispersion in water. A base washing step using 0.01M NaOH initially produced a yellow/brown filtrate, the washing was continued until the filtrate was colourless. The resulting CNT dispersion was then washed with distilled water until pH neutral. Finally, the product was washed with 0.01M HCl, then washed until pH neutral with distilled water. This process not only cleans the

surface of the CNTs and removes much of the amorphous debris, but it also enables some modifications to be carried out by facilitating the formation of a more stable aqueous solution.

To remove any residual acid groups on the surface of the CNTs a vacuum annealing process was undertaken; The CNTs were placed into a tube furnace and heated to 1100°C for 4 hours under vacuum. After the annealing process the MWCNTs were no longer as readily soluble in water due to desorption of polar groups from the surface of the outer walls which were introduced during the growth and purification process. An ultrasonic probe tip was used in combination with an ultra sonic bath to disperse the CNTs. These processes shorten the length of the CNTs and cause an increase in defects seen in the tube walls. The resulting suspension was only stable for a few hours. After purification a platinum additive was introduced to a sample of the CNTs, by mixing an aqueous solution of KPtCl₄ with an aqueous suspension of purified CNTs. The suspension was then rapidly dried in an oven. The ratio of carbon to platinum was 98 to 2wt%. The

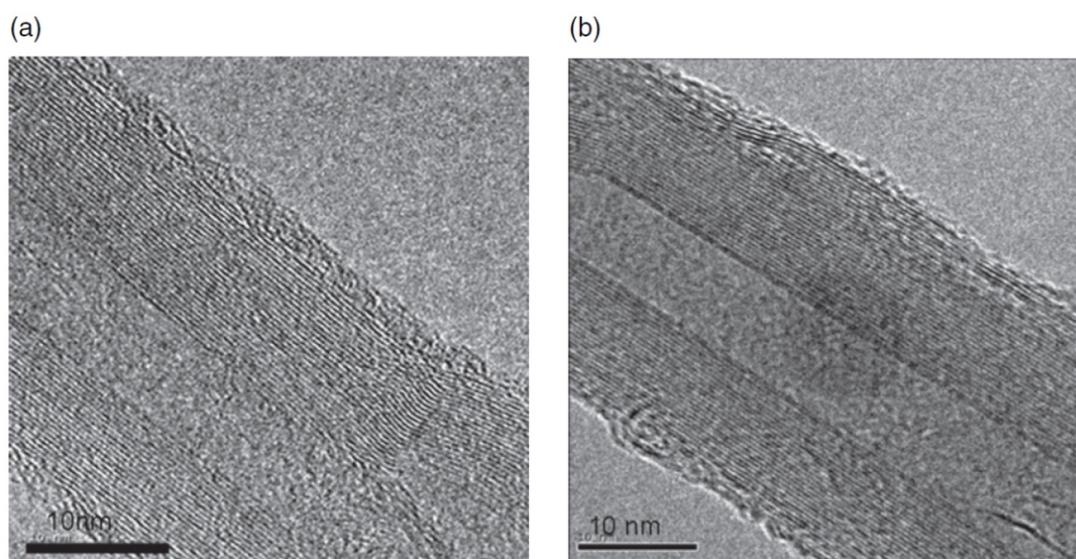


Fig. 2 TEM images a before and b after purification and vacuum annealing

platinum salt was then reduced to the metal by reduction under hydrogen: The dried CNT/Pt salt mixture was placed into a tube furnace which was heated to 100°C for 20 minutes under a flow of argon with 10% hydrogen. Small particles between 1 and 5 nm in diameter were formed on the outer tube wall as observed by TEM (Fig. 3). The Pt particles were well separated with very little visible agglomeration of particles seen. Figure 4 shows the size distribution of the Pt particles.

2.3. Sensor Device

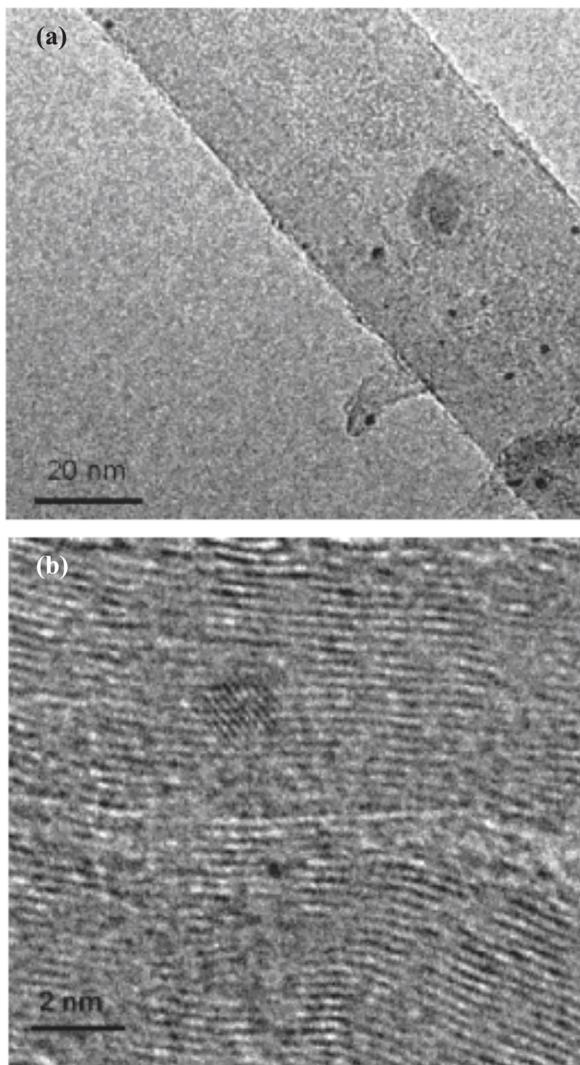


Fig. 3 a TEM image of Purified MWCNT decorated with a catalytic platinum additive at 2wt%. b High magnification image of a Pt particle

The resistive sensor device consisted of gold interdigitated microelectrodes with spacing of 5μm on SiO₂/Si (fabricated at CNM, Spain) which were glued to a ceramic (Al₂O₃) substrate, with a thin resistive-type Pt heater wire, to enable heating of the sensor device (Fig. 5). The ceramic heater was mounted on to a 16 pin header with gold plated contacts. The heater is suspended above the header to enable rapid changes in temperature to be made. A Pt100 temperature sensor was also mounted onto the ceramic heater for control of the operating temperature. The interdigitated microelectrodes are bonded through gold wires to gold contacts on the pins of the header.

2.4. CNT Deposition on to Gold Microelectrodes

Aqueous solutions (containing 0.01 μl of 1 mg in 100ml) of modified CNTs were deposited on to the gold microelectrodes and collected between the electrodes by dielectrophoresis with an alternating current of 1MHz frequency and a peak to peak voltage of 0.6V.

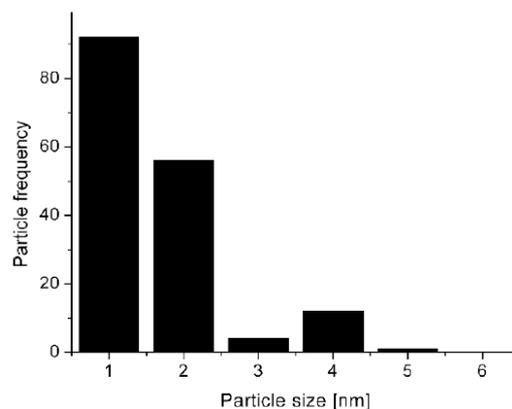


Fig. 4 Size distribution of platinum particles

SEM images showed that the MWCNTs were not aligned as SWCNTs have been shown to be in such a field [10], but became trapped in areas of high field before drying occurred (Fig. 6a). This was also

observed by Suehiro et al. [16]. Earlier experiments where electric fields were not applied did not give conductivity even if the concentration of the solution was increased dramatically. SEM images showed that under these conditions the CNTs dried in a ring pattern around the edge of the droplet and did not bridge the electrodes (Fig. 6b).

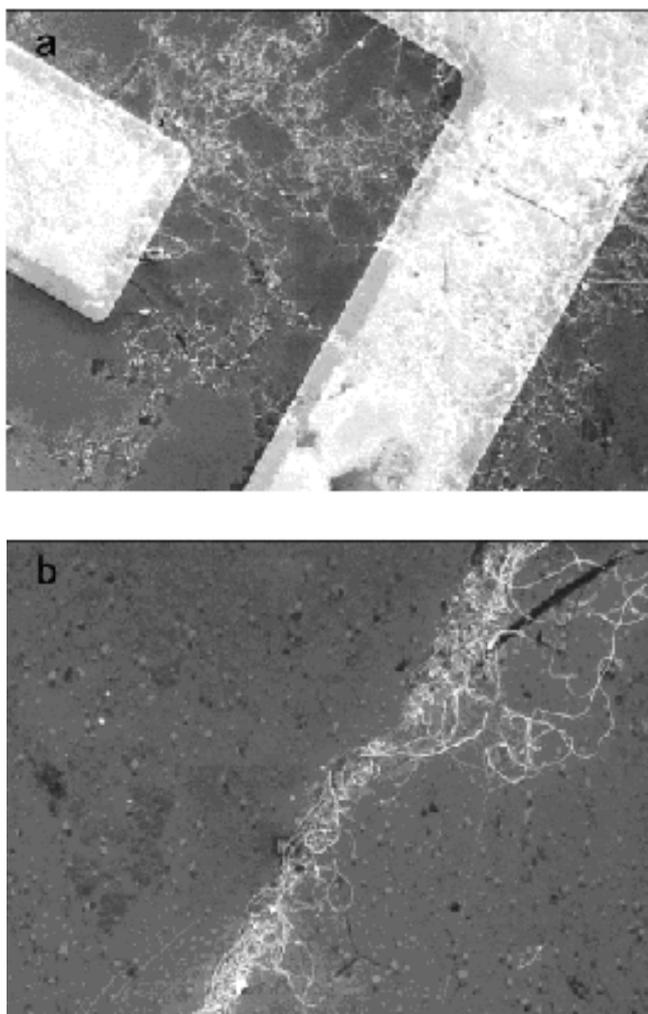


Fig. 6 (a) SEM image of Purified MWCNTs trapped in areas of high field between electrodes, (b) purified MWCNTs dried in a ring around the edge of a droplet

2.5. Gas Measurement Equipment

The headers were mounted into an aluminum gas test chamber with a small 1 cm^3 gas cavity connected to a gas flow line. A computer controlled gas mixing

system using Labview was used to control the gas flow over the sensor. The gas flow was maintained at 100 ml/min throughout the tests and synthetic air was used as the carrier gas. Power was supplied to the sensor with a source meter (Keithley 2601) and the data was processed using Labview. Temperature was controlled using the Pt100 temperature sensor bonded directly on to the ceramic heater near to the Si substrate, power was supplied to the Pt100 by a regulated DC power supply (Kenwood) and the resultant resistance of the Pt100 was measured with a multimeter (Fluke 8840A).

3. Results and Discussions

The sensors were sequentially exposed to NO_2 , CO , NH_3 , and H_2 , at 25, 100 and 500 ppm. The pulses of test gas were 1200 seconds (20 minutes) in duration. The carrier gas (dry air) was pulsed before and after each test gas pulse for 3600 seconds (1 hour). The gas flow was maintained at 100 ml/min thorough out the tests. The same gas test sequence was repeated at operating temperatures of 40, 100 and 200°C .

3.1. Response of Purified Sensor

Figure 7 shows the typical sensitivities ($(R_{\text{TESTGAS}} - R_{\text{AIR}})/R_{\text{AIR}}$) 100 of the purified but otherwise unmodified MWCNT sensor to the test gases at 40, 100 and 200°C . The sensor shows sensitivity to both electron withdrawing and electron donating gases CNTs being amphitricha in nature, with NO_2 demonstrating the greatest sensitivity. It can be generally observed that for NO_2 and CO increasing the temperature increases the magnitude of response, whereas an increase in temperature appears to lead to a decrease in the magnitude of response for NH_3 ,

Sensing occurs in CNTs by an alteration of the density of states close to the Fermi level. MWCNTs are semimetallic and so do not have a band gap, however the valence and conduction band of graphene narrow as they near the Fermi level, forming a Fermi point at which the density of states is zero. This means that even a small change in the Fermi level will have a large effect on the conductance of a sample.

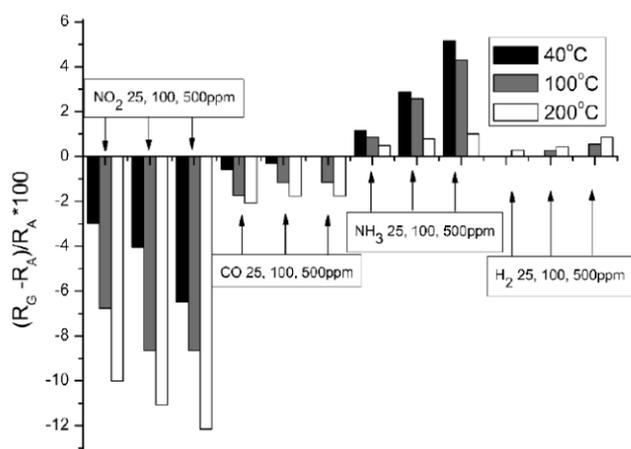


Fig. 7 Response of purified MWCNT sensor to NO₂, NH₃, CO and H₂ at 25, 100 and 500 ppm in air at 40, 100 and 200°C

3.2. Response of MWCNT Sensor with Pt Additives

The same test gas series was then applied to the MWCNT sensor with Pt additives at 2wt% see Fig. 8. The response of the sensor with Pt additives appears similar to the purified sensor with responses seen to all gases however, some differences due to the Pt additive can be seen, and these will be discussed for each gas in turn. Catalytic metal additives are added to increase the sensitivity and decrease the temperature at which the sensitivity maximum is observed. Catalytic metal additives are thought to have two possible mechanisms of altering the sensor response of a metal oxide sensor [3], and these methods may be applicable to a CNT based sensor. The first method is an electronic method

whereby the catalytic additives change their oxidation state on encounter with a gas, and all reactions take place on the metallic particles, in the case of CNT sensors, the CNT would then have a role only as a transducer. The second method of altering a sensor response is by a chemical mechanism, platinum is thought to work via this chemical mechanism [2]. In this method, the additives increase reaction rate by first absorbing the gases then in the case of a CNT sensor transferring them on to the CNT walls. Kong et al. [7] were the first to add metal particles to their CNT sensors. They decorated an individual SWCNT FET device with Pd particles to improve the response towards H₂, claiming that as-prepared SWCNTs were insensitive to this gas, the mechanism which was used to explain this sensing was molecular dissociation of H₂ to H atoms on the Pd surface which then dissolve into the Pd particles, lowering the work function of the metal and transferring electrons to the p-type CNT.

3.3. NO₂ Sensitivity

The purified sensor's response to NO₂ is seen to increase with temperature. At 40°C the response of the two sensors is very similar in magnitude (See Fig. 9). With increasing temperature the purified sensor continues to demonstrate an increase in sensitivity whereas the sensor with Pt additives does not show the same increase at 100°C as is seen for the purified sensor. At 200°C a decrease is seen in the sensitivity of the sensor with Pt additives as the sensitivity decreases below the value at 40°C. With increasing temperature the differences in sensitivity between the two sensors increases as the platinum particles become more catalytically active at higher temperatures. Contrary to the expected increase in sensitivity with addition of

catalytic metal additives a decrease in sensitivity is seen with the addition of Pt decoration. The recovery time after NO_2 exposure is improved for the Pt decorated sensor with increasing temperature. For the purified sensor, an improvement is seen from 40 to 100°C however on increase in temperature to 200°C a smaller percentage recovery is seen. The percentage recovery is very similar for the purified and Pt decorated sensor at 40°C , slightly faster recovery is seen for the Pt decorated sensor at 100°C , and at 200°C the percentage recovery is much greater for the Pt decorated sensor than for the purified sensor. This again indicates that the Pt particles do not play an active role in sensing at room temperature. On running the Pt decorated sensor at higher temperatures there is a trade off between faster response times but lower sensitivity.

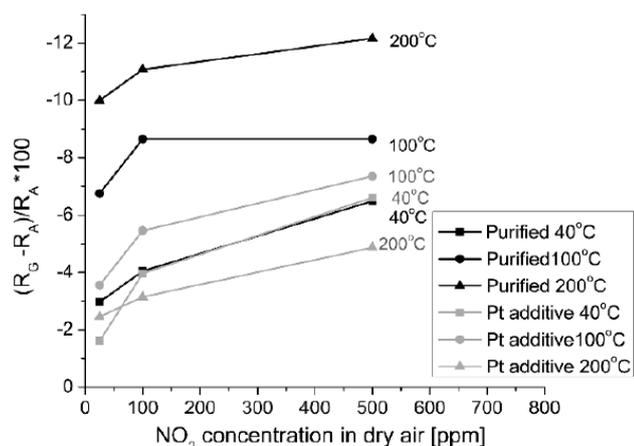


Fig. 8. NO_2 response of purified MWCNT sensor and MWCNT sensor with Pt additive

3.4. NH_3 Sensitivity

The most striking difference in the response towards NH_3 between the two sensors is at 200°C , where the response of the purified sensor appears to almost disappear. A small decrease in response is also seen at 100°C . This reduction in sensor response at 200°C is probably due to weak physisorption of

the NH_3 molecule becoming unfavorable at this temperature. Theoretical simulations have suggested that there is no binding affinity between a CNT and an NH_3 molecule [8], however NH_3 is known to interact strongly with preabsorbed oxygen on graphite [4], and IR studies found that heating under vacuum reduced the NH_3 absorption on SWCNTs, but heating in air regenerated the NH_3 absorption [5]. Contrary to the response of the purified sensor, it is seen that for the Pt decorated sensor NH_3 response does not decrease drastically with temperature. At 40°C the response is similar in magnitude to that at 40°C for the purified sensor, which indicates that the Pt particles are not playing an active role in the sensing at this temperature. At 100°C the response is very similar in magnitude as it was at 40°C , and at 200°C a slight decrease in magnitude of response is seen, however the response at 200°C is much greater than that of the purified sensor, so a different sensing mechanism appears to be operating at higher temperatures. At elevated temperatures the physisorption sensing mechanism of the NH_3 may be replaced by dissociative adsorption and hydrogen abstraction on the Pt nanoparticles decorating the tube walls [11]. This increase in catalytic type behavior of the Pt particles at 200°C is supported by the increase in the sensing of hydrogen seen for the Pt decorated sensor at higher temperatures see Sect. The recovery times for NH_3 are long at lower temperature with very little recovery seen for both the Pt decorated and the purified sensor at 40°C during the hour recovery under air. These long recovery times have also been reported by Kong et al. [8]. At 100°C there is a small improvement in recovery times for both the Pt decorated and purified sensor. At 200°C the response for the purified sensor is very small and does not recover

during the recovery period, and appears to have permanently changed the resistance of the sensor, this may be caused by NH_3 chemisorbing at defect sites on the MWCNT walls. For the Pt decorated sensor at 200°C the recovery is improved with a recovery of approximately 90% for a pulse of 500 ppm concentration.

3.5. H_2 Response

Figure 11 shows the response of the sensors towards hydrogen. The H_2 response is small but comparable in magnitude for both sensors at 40 and 100°C , indicating that the Pt particles are not playing a large role in the H_2 detection at lower temperature. The Pt decorated sensor response to hydrogen is much greater than that of the purified sensor at 200°C , indicating that at this temperature the mechanisms of sensing are different and the Pt particles are playing a much greater active role.

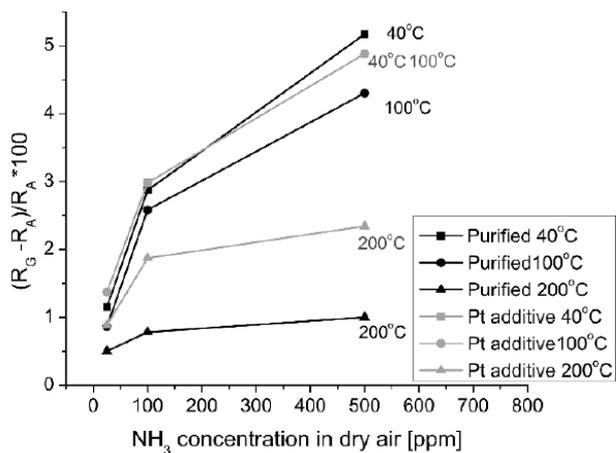


Fig. 9 NO_2 response of purified MWCNT sensor and MWCNT sensor with Pt additive

Dissociative absorption of hydrogen on the Pt particles is likely to be a favourable mechanism at this temperature. After dissociation on Pt nanoparticles H_2 is thought to then spill over on to defect sites on the MWCNT wall. The sensing of hydrogen

with MWCNTs without metal additives does not have an immediately obvious mechanism, however H_2 is thought to adsorb on defect sites on acid treated SWCNT walls [9]. The H_2 may dissociate at defect points on the CNT walls. The recovery time of both sensors to H_2 is greatly improved with temperature. At 200°C the recovery time is around 5 minutes for the Pt decorated sensor and 10 minutes for the purified sensor.

3.6. CO Response

The CO response (Fig. 12) does not scale with concentration, the response decreases with concentration from 25 to 100 ppm. It is also seen that the purified sensor shows a greater response to CO than the Pt decorated sensor. MWCNTs have been reported to show no sensitivity towards CO [13], however graphene sheets have recently shown a small increase in resistance on exposure to CO [14].

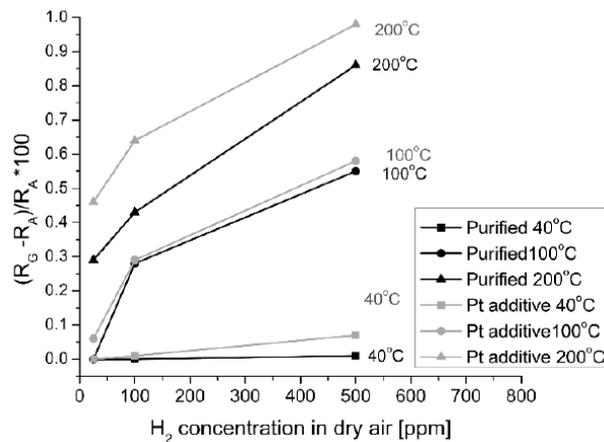


Fig. 10 NH_3 response of purified MWCNT sensor and MWCNT sensor with Pt additive

A further investigation into whether the CO response was in any way affected by the previous exposure to NO_2 was undertaken; The sensors were heated in air at 200°C for 48 hours, then exposed to the test gases at 200°C in the opposite order to remove

the effect that pre-adsorbed NO_2 which may have remained from earlier test pulses. After long desorption times ≥ 48 hours the MWCNT sensor with Pt additives shows a small increase in resistance upon exposure to CO, this response does increase with concentration. After re-exposure to NO_2 the sensor resumes its previous response of a large decrease in resistance upon exposure to CO.

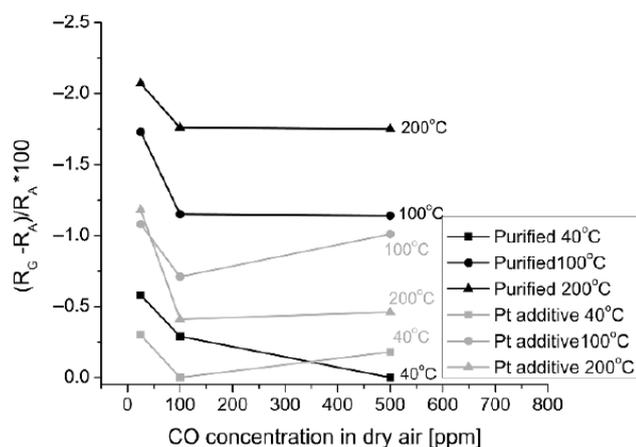


Fig. 11 H_2 response of purified MWCNT sensor and MWCNT sensor with Pt additive

For the Pt decorated sensor, this shows that the CO response is dependant on the previous gas environment. The experiment was repeated with the purified sensor; a small decrease in response was always seen upon exposure to CO. After very long desorption times of several days, the response to CO became very small, but never reversed in direction. The mechanism of sensing for the Pt decorated sensor is likely to be oxidation of the CO to CO_2 over the Pt particles causing the reduction at the platinum particles, and so gain in resistance of the Pt decorated MWCNTs. CO has been detected at 0% humidity with Pt impregnated SnO_2 sensor with a maximum sensitivity at around 200°C [3].

4. Conclusions

MWCNT were synthesised by a CVD method and then decorated with Pt at 2 wt%. The MWCNTs were then drop deposited on to interdigitated gold microelectrodes, and trapped in the high field areas by dielectrophoresis. The sensitivity to a test gas series consisting of NO_2 , NH_3 , CO and H_2 at concentrations varying between 25 and 500 ppm was investigated at 40, 100 and 200°C . The temperature at which the largest difference between the two sensors was seen was 200°C where it is seen that the Pt particles are more active. At lower temperatures there is less difference seen between the two sensors, indicating that the Pt particles play less of an active role. It is likely that there are many competing sensing mechanisms at any temperature for each gas. In the case of NH_3 the physisorption begins to become unfavorable with temperatures above 40°C , and for the Pt decorated sensor, it is thought that a hydrogen abstraction mechanism takes over as the dominant sensing mechanism. For the other test gases the effect of the platinum is seen to improve the speed of recovery, as Pt acts catalytically to increase the reaction rate, which is seen with both H_2 and NO_2 . Cross sensitivity is an issue for CNT sensors and, as has been shown here, the response of the MWCNT sensors does depend on the gas environment to which the CNTs have previously been exposed.

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