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Tailoring of DWNTs for formaldehyde sensing through encapsulation of selected materials

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Tailoring carbon nanomaterials for specific applications is of great importance in the quest to improve the properties of these materials and hence increase their functionality. Using a simple and easy to apply technique Zinc, Zinc oxide and Iodine were encapsulated and confined within double walled carbon nanotubes whose internal diameter ranges from 1.2 to 2.5 nm. The simultaneous confinement of Zinc and Iodine was shown to improve the sensitivity by 100 times while at the same time enhancing the selectivity of DWNTs towards

formaldehyde. By exploiting the p-doping effect of Iodine, CNTs networks were engineered to differentiate formaldehyde from ethanol and acetone, some of the common volatile organic compounds. The ability to tune the chemical selectivity and sensitivity of carbon nanotubes based sensors through inner encapsulation of a specific material thus appears as a new possible route compared to more conventional outer surface functionalization.

1 Introduction: Formaldehyde is one of the most common and well known indoor air pollutants [1]. It has also been classified as a group one carcinogen for human beings even at low concentration of 0.1 ppm and yet it is found in many household products such as cleaning and building materials [2-4]. There is therefore a need for a cheap, sensitive and selective, sensor that can be used for real time monitoring of this volatile organic compound in houses and factories.

Carbon nanotubes have emerged as potential good candidates for the fabrication of cheap chemo-resistive sensors for room temperature gas sensing [5]. This is because of their intrinsic electrical properties and their large specific surface area making them sensitive to gas molecules adsorption.

Their easy integration at the nano- scale makes them ideal for large sensor array miniaturisation. However, despite these positive attributes, metallic CNTs still suffer from poor selectivity and stability when compared to metal oxide based gas sensors [6]. Furthermore pristine CNTs have been shown to be poorly sensitive, when compared to metal oxides [7]. The gas sensing mechanism and selectivity of pristine CNTs is somewhat complicated because of a number of issues such as the mixture of semiconducting and metallic tubes, resulting in resistance modulation due to the different inter-tube junctions and different charge carrier mechanisms such as hole (p-type) and or electron (n-type) transport. Another factor is the wide varying levels of defect states due to different purification methods. The sensitivity of pristine CNTs can however be improved greatly by either surface functionalisation

or metal incorporation or encapsulation as has been shown by many researchers [8-11]. Vanadium encapsulated in multi-walled CNTs with 10 to 15 inner walls was shown to improve the sensitivity by about 1.5 % [12]. This suggests that using CNTs with fewer walls such as single, double or triple walled CNTs would induce an even higher sensitivity improvement. This is expected because the indirect gas interaction with the encapsulated metal would be greater. In this work we propose to investigate the role of selected compounds, encapsulated inside double walled CNTs (DWNTs) with the objective to tailor them for Formaldehyde gas detection.

Metal oxides have been the dominant material of choice for chemo-resistive sensors because of their high sensitivity and stability but their drawback is the need to operate at high temperatures (between 120 to 300 °C) in addition to the slow response/recovery times when compared to CNTs [13-15]. Zinc oxide in particular has been one of the most popular materials for designing gas sensors and is able to detect low levels of formaldehyde down to 1 ppb with "detectable response" of 7.4 (ratio of electrical resistance with and without gas) [16]. Therefore it makes sense to suggest that a combination of DWNTs and ZnO materials would make a good sensor combining high level of sensitivity, fast response and recovery times, able to work at room temperature. This is the main hypothesis tested in this work.

Encapsulating metals in CNTs can boost electronic transport in CNTs without reducing the carbon active sites at their surface responsible for their sensitivity [17-19]. In other previous works (Ref 12), it has been shown that metal and /or metal oxide encapsulation increases the density of states around the Fermi level, which helps to improve sensitivity. The tuneable density of states and the extended π –

conjugation bonding in CNTs (which accounts for most of their electronic properties) makes it possible to tailor the gas adsorption properties of CNTs. Furthermore confinement of metal oxides at nanometer scale inside, 1D spaces is expected to promote new and original phases of the material [20] which in some way may enhance selectivity as certain phases should respond better to certain gases than others. More work on this aspect is still on-going [21]. In this work we however focus on improving the sensitivity of DWNTs towards gases by encapsulating Zinc and Zinc oxide inside the tubes. We also attempt to tune the selectivity by introducing Iodine into the ensemble, which results in p- doping of the CNTs making possible semiconducting tubes to exhibit metallic behaviour at room temperature.

In a nutshell this work highlights our attempts to tailor DWNTs so that they can be used as sensitive and selective sensors of formaldehyde vapour. From high resolution TEM and STEM, EDX, XPS as well as electrical resistance measurements, the influence and role of Zinc and / or Zinc oxide or Iodine encapsulated in DWNTs is discussed. We assess the selectivity aspect by comparing the response of our material to other gases vapours such as ethanol and acetone. This article is organised as follows, section 2 details the experimental setup. In section 3.1, we present the results from the structural characterisation of the material while the results on the vapour sensing in nitrogen atmosphere are discussed in section 3.2. The last section discusses gas sensing in air, and illustrates the competition between n-type and p-type conductivity in DWNTs that occurs in air. After this some discussion on selectivity is presented. We also give a brief discussion on the sensing mechanisms that strongly

consolidates the results. The article concludes by some general discussion on future work.

2 Experimental

2.1 Synthesis and filling of DWNTs

Double walled carbon nanotubes were synthesized as described in Ref [22]. Molten Zinc compounds were used to fill the DWNTs after synthesis as outlined in Ref [23]. One batch was filled using Zinc acetate (bought from Sigma Aldrich) producing Zinc and / or Zinc oxide filled DWNTs after an appropriate heat treatment [23], while another one was filled by Zinc iodide (ZnI_2) (also bought from Sigma Aldrich) likely resulting in a mixture of ZnI_2 , ZnO and possibly iodine filled DWNTs. The last batch contained DWNTs filled with only Iodine as follows: solid Iodine was mixed with raw DWNTs in a mortar in the ratio 3:1 respectively. The mixture was sealed under vacuum in an ampoule after nitrogen purge. The sealed ampoule was heated from room temperature ($25\text{ }^\circ\text{C}$) at $5\text{ }^\circ\text{C}/\text{min}$ until $143\text{ }^\circ\text{C}$ and held at this temperature for 24 hours. It was cooled at a slow rate of $0.1\text{ }^\circ\text{C}/\text{min}$ and then washed in absolute ethanol until the filtrate was colorless.

2.2 Fabrication of sensing devices The sensor devices were fabricated by liquid stencil lithography using PDMS (Poly-DiMethylSiloxane) stencils and liquid phase pipetting of a suspension of the DWNTs of interest in ethanol. To remove the organic solvent, the deposited films were heated at $80\text{ }^\circ\text{C}$ for 30 min in an oven. To ensure repeatability and reproducibility of the devices a constant concentration of 0.1 mg/L of CNTs in ethanol was used.

The PDMS stencil was previously aligned on gold microelectrodes deposited on oxidised silicon substrates by conventional optical lithography and lift-off

process. Each device ($1\text{ cm} \times 2\text{ cm}$) is equipped with a set of 7 DWNT based resistors. Each resistor can accommodate a different suspension of DWNTs (either obtained from pristine DWNTs or from filled DWNTs using the different compounds previously mentioned), allowing a multiplexed (up to 7) detection see diagram Fig 1. Four different devices were tested per each sample batch. Formaldehyde, ethanol, acetone and water vapors, were used as the gases for two probe resistance measurements which were performed at room temperature using the setup illustrated in Fig.1. As shown in figure 1 the different gases injected inside the sensing chamber were obtained after controlled bubbling of a gas carrier (dry Nitrogen or Air) inside an aqueous solution of controlled concentration. The liquid solutions used in our experiments were brought from Sigma Aldrich and used in their absolute state with at acetone and ethanol at 99.95% and 99.98% purity respectively. However formaldehyde was intentionally diluted in deionized water at volume concentration of 0.04g/L or 0.004g/L .

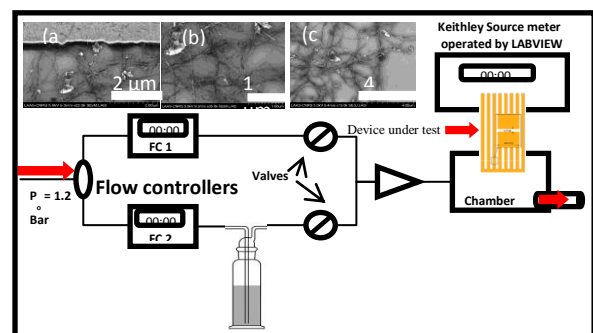


Fig 1: Illustration of the gas sensing system with LABVIEW software used for controlling the Keithley source meter and recording the data. Inset, a,b and c, typical SEM micrographs of sensing area of the device showing (a) the connection of DWNT networks to the gold electrode and (b, and c) entangled DWNTs between electrodes at different magnifications.

3 Results and Discussions

3.1 Structural and elementary characterisation

After synthesis and purification of the four kinds of DWNTs, structural characterisation of the nanotubes was performed using High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Transmission Electron Microscopy (STEM) performed using a JEOL cold-FEG JEM-ARM200F operated at 200 kV and equipped with a probe Cs corrector reaching a spatial resolution of 0.078 nm. EDX spectra were recorded on a JEOL Centurio SDD detector from which we obtained an estimate of the elementary mass composition of the filled CNTs. SEM imaging was done using a Hitachi S - 4800. Figure 2 shows the HRTEM images of unfilled and filled DWNTs.

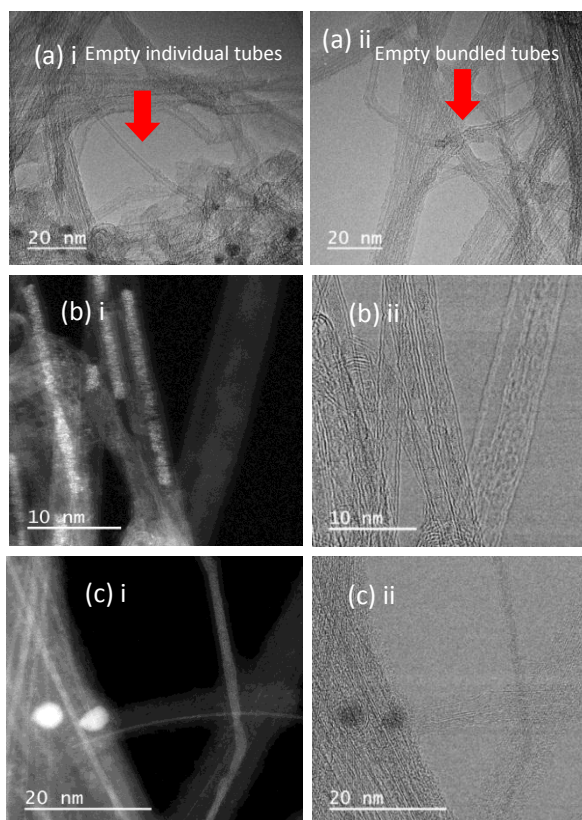


Fig 2: (a) (i and ii) HRTEM images of empty DWNTs showing individual and bundled DWNTs (b) STEM (i) High-angle annular dark field (HAADF) image of Zinc Acetate filled

DWNTs showing high rate of filling and (ii) the corresponding bright field (BF) image. (c) (i) HAADF image of Zinc iodide filled DWNTs showing a high filling rate and the corresponding (ii) bright field image. The filling material appears as white spots in the dark field images due to the high electron density of the filler material compared to carbon. The large bright spots on C(i) is from the catalyst material.

Careful TEM characterisation at high magnification revealed that the filler material is not crystalline but rather appears amorphous. The Zinc Iodide filled DWNTs had longer chains of Zinc and Zinc oxide, in addition to very short chains of what was observed previously to be Iodine chains [24].

STEM-EDX analysis showed that the Zinc acetate filled DWNTs exhibited mainly Zinc and Zinc oxide as the filler material as shown in Fig 3, while the ZnI_2 filled sample exhibited Zinc, Zinc oxide and Iodine / Zinc iodide, the copper that appears on the spectrum is from the TEM grid.

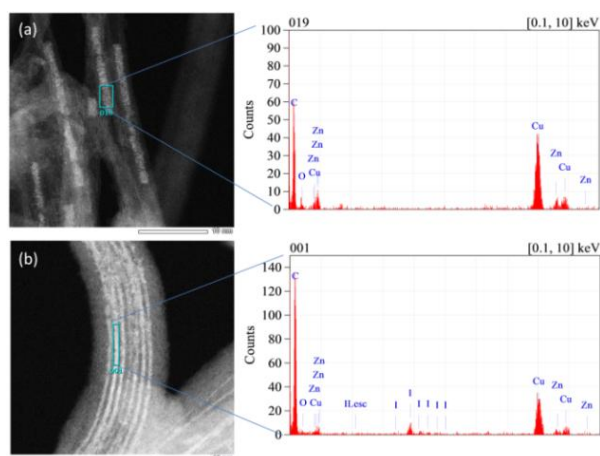


Fig 3: HAADF-STEM image and EDX analysis of the filled DWNTs (a) Zinc acetate filled DWNTs (b) Zinc iodide filled DWNTs.

Table 1, summarizes the elementary composition of the filled CNTs and it shows that Zinc content in ZnI_2 filled DWNTs is less compared to that in Zinc acetate filled DWNTs. This probably has a significant effect on the sensitivity of the material as shall be discussed later.

Table 1 Elementary composition of the filled DWNTs, obtained by EDX as an average of data from three different spots probed with same number of counts.

Element	Zinc acetate Filled DWNTs Mass %	Zinc Iodide Filled DWNTs Mass %
C	93.1	89.3
O	1.8	0.7
Zn	4.3	1.8
I	(Not Present)	6.3

The identity of the filler material was further confirmed using XPS, see Fig. 4(a and b). From Fig. 4(b (i)) the unusual double peak of the O1s, suggest that the Zinc is in the Zn(OH)₂ environment, but more studies are needed to confirm this hypothesis [25]. The presence of the Auger peak associated with the Zn2p peak at 992 eV might be taken as an indication of Zinc buried under carbon supporting the HRTEM analysis which confirmed that the Zinc is encapsulated inside CNTs.

3.2 Gas response in Nitrogen atmosphere

After confirming the identity and the amount of the filler material, two probes electrical resistance measurements were performed at various mass concentrations of formaldehyde and other volatile gases ranging from 1.8 to 4 % as calculated using equation 1. The vapour to be detected was diluted in nitrogen gas or dry synthetic air and its relative concentration was controlled by adjusting the mass flow rate in the different branches of the experimental set-up shown in figure 1. The percentage mass concentration (C %) was calculated using equation 1.

$$C = \frac{P_i}{P} * \frac{f}{f+F} * 100\% , \text{ where the symbols stand}$$

for

$$P_i , \text{ the partial pressure of the vapour at } 25^\circ\text{C},$$

$$P, \text{ the total input pressure which was kept at } 1.2 \text{ Bar},$$

f , the mass flow rate inside the bubbling branch,
 F , the mass flow rate inside the pure gas carrier branch.

The sensor's response is defined as $\frac{R_p - R_o}{R_o} \times 100$, where R_p is the resistance in the presence of the vapour, while R_o is the resistance in the carrier gas (air or nitrogen). In most of the discussions the sensor's response was used instead of the actual resistance (nonetheless highlighted in the supplementary data, Fig. S1) so as to enable easy comparison of the different samples. As a matter of fact, CNT network devices are well known to have different resistance values due to non-uniformity, which justifies the use of response for easy comparison.

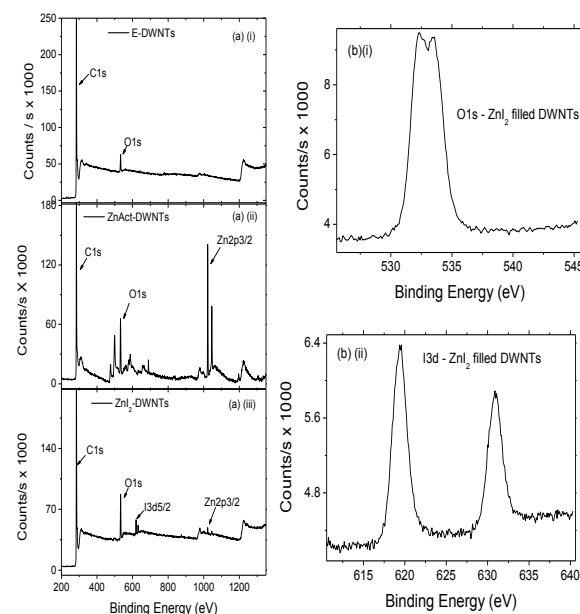


Fig 4: (a)(i) XPS survey spectra of raw DWNTs (ii) XPS survey spectra of Zinc acetate filled DWNTs (iii) XPS survey spectra of Zinc iodide filled DWNTs (b) (i) The O1s peaks of ZnI₂ filled DWNTs (ii) The I3d peaks for iodine filled DWNTs.

To understand the influence of the filler material on the gas response to formaldehyde, the response to formaldehyde vapour for the three samples (unfilled DWNTs, labelled as E-DWNT on the figures, Zinc

acetate filled (labelled as ZnAct-DWNT) and Zinc iodide filled (labelled as ZnI₂-DWNT) was measured firstly in nitrogen atmosphere, to avoid the complications due the p-doping of CNTs that is likely to occur in air. Before measurements, nitrogen gas was flushed into the sample chamber for 10 minutes. After nitrogen flushing for 10 mins, the formaldehyde vapour was introduced into the chamber for approximately 180 s.

It was observed that in nitrogen atmosphere, Fig. 5(a), the response for Zinc acetate filled DWNTs and Unfilled DWNTs samples, increased upon formaldehyde vapour introduction, while for the Zinc Iodide filled nanotubes it decreased.

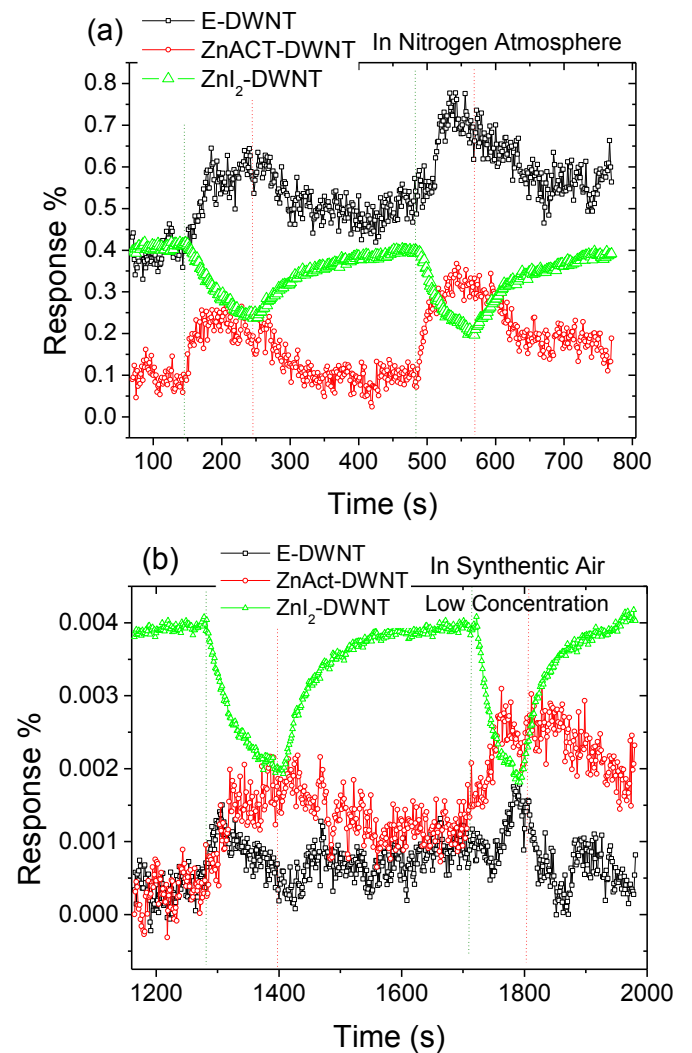


Fig 5: (a) Formaldehyde gas response of the three kinds of DWNTs measured in nitrogen atmosphere. (b) Formaldehyde gas response of the three kinds of DWNTs measured in synthetic air atmosphere. In both cases, during the first cycle the vapour mass concentration was 1.8 % as calculated using equation 1 and this was increased to 2.2 % during the second cycle by increasing the flow rate of the carrier gas. The olive green dotted vertical lines show when the respective vapour was introduced and the red lines indicate when the vapour was closed.

Corresponding resistance changes are shown in the supplementary data. This suggests that the sensing mechanism in Zinc Iodide filled nanotubes is different from that in Zinc acetate filled and the unfilled DWNTs. In our attempt to find a plausible sensing mechanism we note that formaldehyde has an

electron affinity of 0.65 eV [26], which means accepting an electron is energetically favourable at room temperature. This means the formaldehyde molecules will draw electrons from the DWNTs resulting in either an increase in resistance (response) if n-type conduction is the dominant transport mechanism or a decrease in resistance (response) when p-type conduction is the dominant mechanism see schematic illustration in Fig.6.

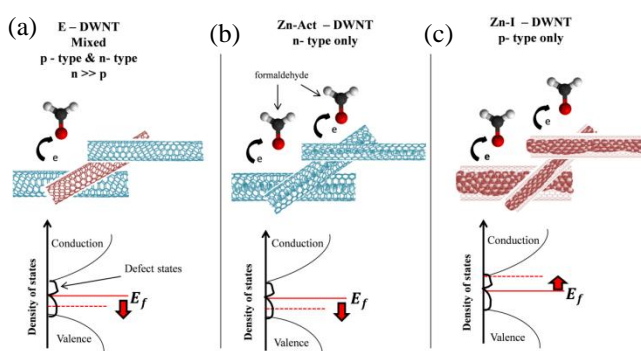


Fig 6: Schematic of the sensing mechanism as envisioned for different DWNTs samples under investigation. An approaching formaldehyde molecule will draw electrons from the DWNTs; this will push the Fermi level (E_f) down when the n-type DWNTs dominate the conduction (a and b) or push the Fermi level up when p-type DWNTs dominate (c).

Since it has already been established that Iodine induces p-type doping of SWNTs, creating charge carriers in the SWNTs walls and as a result, the semiconducting SWNTs become metallic, while metallic SWNTs become even more metallic due to increased density of carriers (holes) [25]. The same effect was evidenced in Iodine doped DWNTs [20, 27, 28], it is therefore logical to assume that Zinc iodide filling results in p-type doping of DWNTs which, explains the decrease in response. The increase in response observed for unfilled DWNTs when formaldehyde was introduced can be explained as follows: unfilled DWNTs are composed of a mixture of semiconducting and metallic DWNTs with the latter being predominant and hence the dominating

conduction is due to electrons (n-type). This assumption is plausible due to the presence of ca. 80 % DWNTs in the sample as well as their wide diameter distribution. The same sensing mechanism is applicable for the Zinc acetate filled DWNTs implying that Zinc acetate filling enhances n-type conduction probably due to high density of electrons from the encapsulated Zinc. Elementary analysis from EDX in table 1 showed that Zinc acetate filled DWNTs have 2.5 % more Zinc by mass compared to Zinc iodide filled DWNTs, which might explain why this effect of Zinc is not observed in Zinc iodide filled DWNTs as Iodine dominates.

3.3 Gas response in synthetic air atmosphere

When the same tests using formaldehyde were performed in synthetic air (Fig. 5(b)), the significant effect of oxygen on CNT sensing mechanism was clearly demonstrated. It was observed that for the unfilled DWNTs, at low vapour mass concentrations of 1.8 and 2.2 % (i.e. first and second cycle respectively of Fig. 5(b)) the response increases initially upon formaldehyde introduction but as more air increases (which is the carrier gas) in the chamber the response begins to decrease whilst still on the same cycle. This is clear evidence of competition between n-type and p-type conductivity. The initial increase in response is due to the dominant n-type conduction in mixed DWNTs but as more air (oxygen) increases in the chamber it p-dopes the DWNTs, resulting in the decrease in response. Increasing vapour concentrations to 2.8 and 3.2 % (i.e. first and second cycle respectively of Fig. S2, supplementary data), results in more air into the chamber. It was observed that the initial increase in response upon vapour introduction disappeared and replaced by a decrease with some small steps in response. This supports the ex-

plained competition mechanism. At high concentrations the p-doping effect of DWNTs by oxygen dominates and hence the decrease in response. As already explained an electron acceptor stimulant gas will push the Fermi level down resulting in an increase in resistance for n-type conductivity and the opposite is true for p-type conductivity as illustrated in Fig. 6 (b and c). Filling the DWNTs with Zinc acetate and Zinc Iodide results in filled DWNTs being predominately n-type and p-type respectively. This explains why the filled DWNTs are not significantly affected by the competition behaviour due to oxygen. However the effect of the air for these filled sensors is observed in the suppressed overall response. In general the nanotube's response to formaldehyde vapour was about 100 times lower in synthetic air atmosphere than in nitrogen atmosphere. It was also noticed that the unfilled and Zinc acetate filled tubes exhibit poor recovery / reversibility. This is highlighted by an increasing baseline with time for these two samples, which is not the case with the Iodine doped samples. Furthermore the Zinc Iodide filled DWNTs exhibited far much better response in air than the other samples as evidenced by the well-defined peaks in Fig. 5(b).

3.4 The role of Iodine on the gas response

To confirm that Iodine and not Zinc was responsible for the doping effect and the peculiar response of the Zinc Iodide filled nanotubes, Iodine only filled DWNTs were also tested with formaldehyde and ethanol and the results confirmed that the peculiar response of Zinc Iodide was likely due to Iodine doping as shown in Fig. 7. As observed earlier the introduction of the formaldehyde vapour results in a decrease in resistance/response for the Iodine only filled DWNTs. This confirms that the gas sensing mechanism for this sample and that of ZnI_2 filled sample is similar. Be-

cause the response of the Iodine (only) filled tubes was weaker we only showed results at higher mass concentration greater than 2.8 % to illustrate the question about the mechanism. We also compared it with the response to ethanol which showed a different sensing mechanism, in which the resistance increases as this was the case with Zinc Iodide doped sample (Fig. 7).

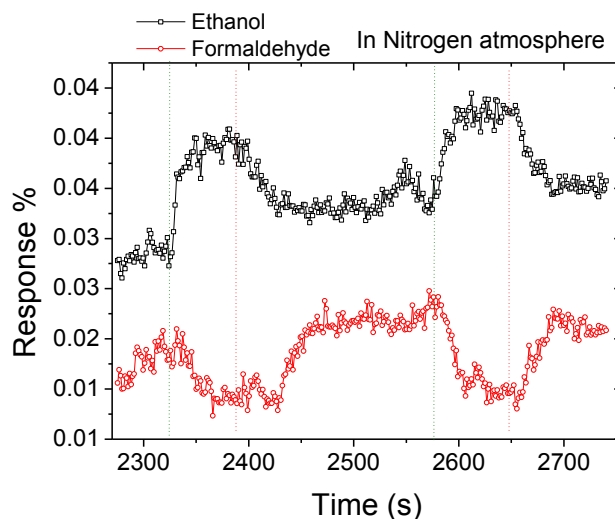


Fig 7: Response of iodine (only) - incorporated DWNTs to 2.8 % mass concentration of ethanol or 3.2 % of formaldehyde in nitrogen atmosphere (as calculated using equation 1). The second cycle is when vapour concentration was increased by 0.4 % by increasing the flow rate of the carrier gas. The olive green dotted vertical lines show when the respective vapour was introduced and the red lines indicate when the vapour was closed.

Figure 8, investigates in more details the changes of sensing mechanism of ZnI_2 filled DWNTs as a function of the stimulant gas (i.e. acetone, ethanol, formaldehyde and water) in nitrogen atmosphere. The stimulant solvents for this particular investigation were used in their original commercial concentration in water solution from the supplier with the exception of formaldehyde that was diluted to 0.04 g/L in water from the original 0.4 g/L.

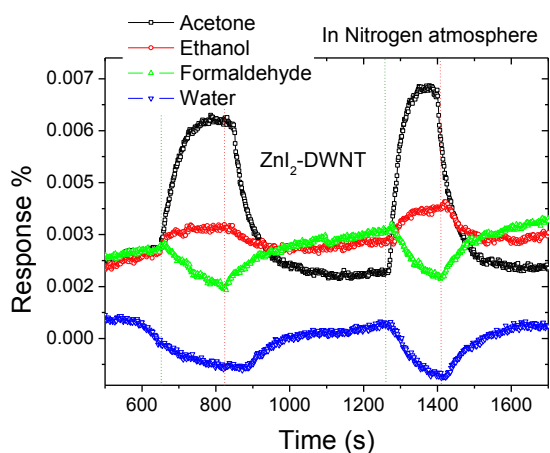


Fig 8: Response of Zinc Iodide filled DWNTs to different common volatile organic compounds (Acetone – 2.3%, Ethanol – 2.1%, Water – 2.0% and Formaldehyde – 2.8% as calculated using equation) in nitrogen atmosphere. The second cycle is when vapour concentration was increased by 0.4 % by increasing the flow rate of the carrier gas. The olive green dotted vertical lines show when the respective vapour was introduced and the red lines indicate when the vapour was closed.

The graph (Fig.8) shows that the response mechanism of the Zinc Iodide - filled DWNTs to ethanol and acetone is different to its response to water or formaldehyde vapour. In this regard this material is exhibiting some selectivity. Ethanol and water are very similar solvents but however the Zinc Iodide - filled sensors showed relative selectivity which we might attribute to the difference in the electron affinities of water (0.8 eV [29]) and ethanol (1.82 eV) [30]. With this background, water vapour then appears as the only competing gas with formaldehyde.

Since formaldehyde was dissolved in water, we then sought to establish if the observed response was due to water or formaldehyde. Different solutions (by concentration) of formaldehyde in water solution were prepared and tested. From Fig.9, the response of the more dilute solutions was higher than for the more concentrated. This observation can be attributed to either the increased volatility of the dilute solutions,

which means that more molecules of the formaldehyde are carried onto the DWNTs by the nitrogen gas or that the higher water content in dilute solutions was increasing the response. However the second argument was then ruled out, when we compared the 0.04 g/L to the 0.004 g/L solution. If the water content was the main driving factor then the 0.04 g/L solution would be expected to lead to a higher response, which is not the case and therefore supporting the first argument. It was nevertheless noted that water vapour tends to stick longer on the DWNTs making the recovery after exposure of the dilute samples poor as shown by the increasing baseline. The 0.4 g/L solution had a very fast recovery rate, suggesting that formaldehyde alone does not absorb firmly on to the nanotubes.

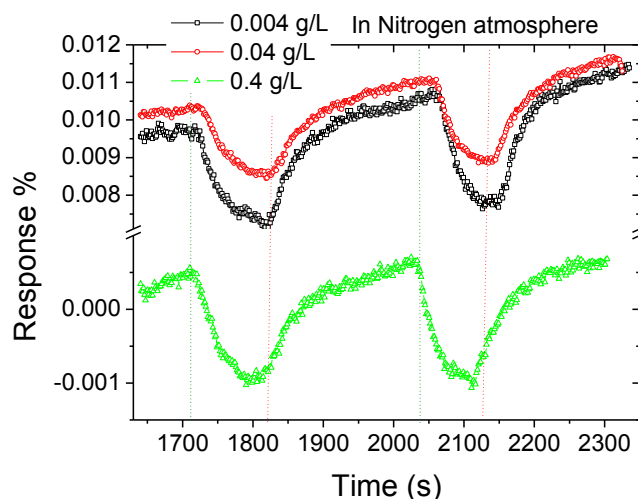


Fig 9: Response of Zinc Iodide filled DWNTs to 2.8 % (as calculated using equation 1) of formaldehyde diluted at different concentrations in deionised water. The second cycle is when vapour concentration was increased by 0.4 % by increasing the flow rate of the carrier gas. The olive green dotted vertical lines show when the respective vapour was introduced and the red lines indicate when the vapour was closed.

Having established the role of the Iodine in the Zinc Iodide filled DWNTs, the next question was then, to investigate the role of Zinc. To answer this question we compared the response of the Iodine only filled

DWNTs to that of zinc iodide filled DWNTs (Fig.7 and 8). From the numerical values of the response it is clear that zinc enhances the response of the nanotubes by two orders of magnitude. This observation is in agreement with previous studies in Ref [12] which demonstrated that metals encapsulated in DWNTs increased the response of the DWNTs due to the possible increase in the density of states around the fermi level of the nanotubes. Another important parameter worth to consider is the stability of the sensor. In this regard it was observed that our sensors were stable within the four months of the experiments. However for commercialisation more dedicated studies on stability and detection limit would be needed.

Conclusions In conclusion, we have managed to tailor or tune the response of DWNTs towards formaldehyde sensing in two ways but using one salt, Zinc Iodide. Filling DWNTs using, Zinc Iodide results in encapsulation of both Zinc and Iodine in the nanotubes. The enclosed Zinc improves the sensitivity by two orders of magnitude while the iodine enhances the selectivity towards formaldehyde by making the DWNT ensemble (network) predominantly metallic from a state of mixture of metallic and semiconducting DWNTs. Our main observation is that metal encapsulation has been shown to be another ideal route to enhance response sensitivity of DWNTs without compromising the response time as there is no direct interaction between the gas and the encapsulated material. It therefore offers an alternative route for manipulating the electronic properties of DWNTs for a desired application. In this regard we have laid a strong foundation for the application of DWNTs in formaldehyde sensing and thus increasing the functionality of the material.

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References

- [1] Y.I. Korpan, M.V. Gonchar, A.A. Sibirng, C. Martelet, A.V. El'skaya, T.D. Gibson and A.P. Soldatkin, *Biosens. Bioelectron* **15**, 77 (2000).
- [2] K.C. Gupta, A.G. Ulsamer and P.W. Preuss, *Environ. Int.* **8**, 349 (1982).
- [3] J.A. Pickreil, B.V. Mokier and L.C. Griffis, *Environ. Sci. Technol.* **17**, 753 (1983).
- [4] J.Y. Kim, J. Lee, S. Hong and T.D. Chung, *Chem. Commun.* **47**, 2892 (2011).
- [5] R. Tang, Y. Shi, Z. Hou and L. Wei, *Sensors* **17**, 882 (2017).
- [6] P.R. Chung, C.T. Tzeng, M.T. Ke and C.Y. Lee, *Sensors* **13**, 4468 (2013).
- [7] W.D. Zhang and W.H. Zhang, *Journal of Sensors* **160698**, 1 (2009).
- [8] J. Wang, L. Liu, S.Y. Cong, J.Q. Qi and B.K. Xu, *Sensors and Actuators B* **134**, 1010 (2008).
- [9] Y. Lu, M. Meyyappan and J. Li, *Nanotechnology* **22**, 055502 (2011).
- [10] D. Shi, L. Wei, J. Wang, J. Zhao, C. Chen, D. Xu, H. Geng and Y. Zhang, *Sensors and Actuators B* **177**, 370 (2013).
- [11] H. Tai, X. Bao, Y. He, X. Du, G. Xie and Y. Jiang, *IEEE Sensors Journal* **15**, 6904 (2015).
- [12] G. Chimowa, Z.P. Tshabalala, A.A. Akande, G. Bepete, B. Mwakikunga, S.S. Ray and E.M. Benecha, *Sensors and Actuators B* **247**, 11 (2017).
- [13] R. Kumar, O.A. Dossary, G. Kumar and A. Umar, *Nano-Micro Lett.* **7**, 97 (2015).
- [14] M.Z. Yang, C.L. Dai and P.J. Shih, *Sensors* **14**, 12735 (2014).
- [15] H. Gu, Z. Wang and Y.Hu, *Sensors* **12**, 5517 (2012).
- [16] D. Chen and Y.J. Yuan, *IEEE Sensors Journal* **15**, 6749 (2015).
- [17] P.V.C. Medeiros, S. Marks, J.M. Wynn, A. Vasylenko, Q.M. Ramasse, D. Quigley, J. Sloan and A.J. Morris, *ACS Nano* **11**, 6178 (2017).

- 1 [18] B.T. Hang, H. Hagashi, S.H. Yoon, S. Okada, J.I.
2 Yamaki, *Journal of Power sources* 178, 393 (2008).
3
4 [19] H. Wu, D. Wexler, A.R. Ranjbartoreh, H. Liu and G.
5 Wang, *Int. Journal of hydrogen energy* **35**, 6345
6 (2010).
7
8 [20] J. Cambedouzou and J.L. Sauvajol, *Phys. Rev.* **B 69**,
9 235422 (2004).
10
11 [21] C. Nie, A-M. Galibert, B.Soula, E. Flahaut, J.
12 Sloan, M. Monthioux, *Carbon* **110**, 48 (2016).
13
14 [22] E. Flahaut, R.Bacsa, A. Peigney and Ch. Laurent,
15 *Chem. Commun. (Cambridge)* **12**, 1442 (2003).
16
17 [23] C. Nie, A-M. Galibert, B. Soula, L. Datas, J. Sloan,
18 E. Flahaut, M. Monthioux, *Transactions on*
19 *Nanotechnology (special Section/Issue on the IEEE*
20 *Nanotechnology Materials and Devices. Conference)*
21 DOI:1109/TNANO.2017.2686434 (22/03/2017).
22
23 [24] G. Atanasova, A. Og Dikovska, M. Stankova, P. Ste-
24 fanov and P.A. Atanasov, *J. Phys. Conf. Ser.* **356**,
25 012036 (2012).
26
27 [25] B.R. Sankapal, K. Setyowati and J.Chen, *App. Phys.*
28 *Lett.* **91**, 173103 (2007).
29
30 [26] J.S. Francisco, J.W. Thoman Jr, *Chem. Phys. Lett.*
31 **300**, 553 (1999).
32
33 [27] T. Michael, L. Alvarex et. al, *J. of Physics and*
34 *Chemistry of Solids* **67**, 1190 (2006).
35
36 [28] A. Zabair et. al, , *Phys. Rev. Mat.* **1**, 064002 (2017).
37
38 [29] A.P. Gaiduk, T.A. Pham, M. Govoni, F. Paesani, G.
39 Galli, *Nature Communications*, DOI:
40 10.1038/s41467-017-02673-2.
41
42 [30] <https://ccdb.nist.gov/elecaff2.asp?casno=67561> (ac-
43 cessed 19 May 2018).
44
45
46
47
48
49
50
51
52
53
54
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56
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