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Tailoring of Double-Walled Carbon Nanotubes 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, increasing their functionalities. Using a simple and easy to apply technique, zinc, zinc oxide, and iodine are encapsulated and confined within double-walled carbon nanotubes (DWNTs) whose internal diameter ranges from 1.2 to 2.5 nm. The simultaneous confinement of zinc and iodine is shown to improve the sensitivity by 100 times while, at the same time, enhancing the selectivity of DWNTs toward formaldehyde. By exploiting the p-doping effect of iodine, carbon nanotube (CNT) networks are engineered to differentiate formaldehyde from some of the common volatile organic compounds, such as ethanol and acetone. The ability to tune the chemical selectivity and sensitivity of CNT-based sensors through inner encapsulation of a specific material thus appears as a new possible route compared with more conventional outer surface functionalization.

1. Introduction

Formaldehyde is one of the most common and well-known indoor air pollutants. It has also been classified as a group one carcinogen for human beings even at a low concentration of 0.1 ppm, and yet, it is found in many household products, such as cleaning and building materials. 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 (VOC) in houses and factories.

Carbon nanotubes (CNTs) have emerged as potential good candidates for the fabrication of cheap chemoresistive sensors for room temperature gas sensing. 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 nanoscale makes them ideal for large sensor array miniaturization. However, despite these positive attributes, metallic CNTs still suffer from poor selectivity and stability when compared with metal oxide-based gas sensors. Furthermore, pristine CNTs have been shown to be poorly sensitive, when compared with metal oxides. The gas sensing mechanism and the selectivity of pristine CNTs are 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 functionalization or metal incorporation or encapsulation as has been shown by many researchers. Vanadium encapsulated in multi-walled CNTs with 10–15 inner walls was shown to improve the sensitivity by about 1.5%. This suggests that using CNTs with fewer walls, such as single-walled CNT (SWNT), double-walled CNT (DWNT), or triple-walled CNT, would induce an even higher sensitivity improvement. This is expected because the in-direct gas interaction with the encapsulated metal would be greater. In this work, we propose to investigate the role of selected compounds, encapsulated inside DWNTs with the objective to tailor them for formaldehyde gas detection.

Metal oxides have been the dominant material of choice for chemoresistive sensors because of their high sensitivity and stability, but their drawback is the need to operate at high temperatures (between 120 and 300 °C) in addition to the slow response/recovery times when compared with CNTs. 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 a “detectable response” of 7.4 (ratio of electrical resistance with and without gas). 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. In other previous works, 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 tunable density of states and the extended \( \pi \)-conjugation bonding in CNTs (which accounts for most of their electronic properties) make 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, 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. In this work, we, however, focus on improving the sensitivity of DWNTs toward 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 behavior 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 vapor. From high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM), energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), and electrical resistance measurements, the influence and role of zinc and/or zinc oxide or iodine encapsulated in DWNTs are discussed. We assess the selectivity aspect by comparing the response of our material to other gas vapors, such as ethanol and acetone. This article is organized as follows. Section 2 details the experimental setup. In Section 3.1, we present the results from the structural characterization of the material, whereas the results on the vapor 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 conductivities in DWNTs that occur 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. This article concludes by some general discussion on future work.

2. Experimental Section

2.1. Synthesis and Filling of DWNTs

DWNTs were synthesized as described in the previous study. Molten zinc compounds were used to fill the DWNTs after synthesis as outlined in the previous study. One batch was filled using zinc acetate (bought from Sigma Aldrich), producing zinc and/or zinc oxide-filled DWNTs after an appropriate heat treatment, whereas the other 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 °C) at 5 °C min\(^{-1}\) until 143 °C and held at this temperature for 24 h. It was cooled at a slow rate of 0.1 °C min\(^{-1}\) 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 polydimethylsiloxane (PDMS) 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 °C for 30 min in an oven. To ensure repeatability and reproducibility of the devices, a constant concentration of 0.1 mg L\(^{-1}\) of CNTs in ethanol was used.

The PDMS stencil was previously aligned on gold microelectrodes deposited on oxidized silicon substrates by conventional optical lithography and lift-off process. Each device (1 cm × 2 cm) was equipped with a set of seven DWNT-based resistors. Each resistor could 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 seven) detection (see Figure 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 shown in Figure 1. As shown in Figure 1, the different gases injected inside the sensing chamber were obtained after controlling the 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 acetone and ethanol at 99.95% and 99.98% purity, respectively. However, formaldehyde was intentionally diluted in deionized water at a volume concentration of 0.04 or 0.004 g L\(^{-1}\).

**Figure 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 with carbon. The large bright spots on (c (i)) is from the catalyst material.
3. Results and Discussions

3.1. Structural and Elementary Characterization

After synthesis and purification of the four kinds of DWNTs, structural characterization of the nanotubes was performed using HRTEM and STEM performed using a JEOL cold-field emission gun (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 silicon drift detector (SDD) detector from which we obtained an estimate of the elementary mass composition of the filled CNTs. Scanning electron microscopy (SEM) imaging was done using a Hitachi S-4800.

Figure 2 shows the HRTEM images of unfilled and filled DWNTs.

Careful TEM characterization 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]

The STEM-EDX analysis showed that the zinc acetate-filled DWNTs exhibited mainly zinc and zinc oxide as the filler material, as shown in Figure 3, whereas the ZnI2-filled sample exhibited zinc, zinc oxide, and iodine/zinc iodide, and the copper that appears on the spectrum is from the TEM grid.

Table 1 summarizes the elementary composition of the filled CNTs, and it shows that the zinc content in ZnI2-filled DWNTs is less compared with 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 the same number of counts.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Zinc acetate-filled DWNTs [mass %]</th>
<th>Zinc iodide-filled DWNTs [mass %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>93.1</td>
<td>89.3</td>
</tr>
<tr>
<td>O</td>
<td>1.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Zn</td>
<td>4.3</td>
<td>1.8</td>
</tr>
<tr>
<td>I</td>
<td>(Not present)</td>
<td>6.3</td>
</tr>
</tbody>
</table>

The identity of the filler material was further confirmed using XPS (see Figure 4a,b). From Figure 4b(i), the unusual double peak of O1s suggests 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-probe 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 vapor to be detected was diluted in nitrogen gas.

![Figure 3. HAADF-STEM image and EDX analysis of the filled DWNTs: a) zinc acetate-filled DWNTs and b) zinc iodide-filled DWNTs.](image)
or dry synthetic air, and its relative concentration was controlled by adjusting the mass flow rate in the different branches of the experimental setup shown in Figure 1. The percentage mass concentration (C%) was calculated using Equation (1).

\[ C = \frac{P_i}{P} \times \frac{f}{f + F} \times 100\% \]  

where \( P_i \) is the partial pressure of the vapor at 25 °C, \( P \) is the total input pressure, which was kept at 1.2 bar, \( f \) is the mass flow rate inside the bubbling branch, and \( F \) is the mass flow rate inside the pure gas carrier branch.

The sensor’s response is defined as \( \frac{R - R_o}{R_o} \times 100 \), where \( R \) is the resistance in the presence of the vapor, whereas \( R_o \) 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 Figure S1, Supporting Information) 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 nonuniformity, which justifies the use of response for easy comparison.

To understand the influence of the filler material on the gas response to formaldehyde, the response to formaldehyde vapor 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 first in nitrogen atmosphere, to avoid the complications due to p-doping of CNTs that is likely to occur in air. Before
measurements, nitrogen gas was flushed into the sample chamber for 10 min. After nitrogen flushing for 10 min, the formaldehyde vapor was introduced into the chamber for \(\approx 180\) s.

It was observed that in nitrogen atmosphere (Figure 5a), the response for zinc acetate-filled DWNTs and unfilled DWNTs samples increased upon formaldehyde vapor introduction, whereas for the zinc iodide-filled nanotubes, it decreased.

Corresponding resistance changes are shown in the Supporting Information. This suggests that the sensing mechanism in the zinc iodide-filled nanotubes is different from that in the zinc acetate-filled and 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 favorable at room temperature. This means that 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 Figure 6).

As 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, whereas 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 \(\approx 80\%\) 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. An elementary analysis from EDX in Table 1 showed that zinc acetate-filled DWNTs have 2.5% more zinc by mass compared with 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 (Figure 5b), the significant effect of oxygen on the CNT sensing mechanism was clearly demonstrated. It was observed that for the unfilled DWNTs, at low vapor mass concentrations of 1.8% and 2.2% (i.e., the first and second cycles, respectively, of Figure 5b), 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 while still on the same cycle. This is a clear evidence of competition between n-type and p-type conductivities. The initial increase in response is due the dominate 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 vapor concentrations to 2.8% and 3.2% (i.e., the first and second cycles, respectively, of Figure S2, Supporting Information) results in more air into the chamber. It was observed that the initial increase in response upon vapor introduction disappeared and replaced by a decrease with some small steps in response. This supports the explained competition mechanism. At high concentrations, the p-doping effect of DWNTs by oxygen dominates and hence decreases 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 shown in Figure 6b,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 behavior due to oxygen. However, the effect of the air for these filled sensors is observed in the suppressed overall response. In

![Figure 5](image-url)
general, the nanotube’s response to formaldehyde vapor 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 Figure 5b.

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 Figure 7. As observed earlier, the introduction of the formaldehyde vapor 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 the ZnI2-filled sample are similar. Because 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 the zinc iodide-doped sample (Figure 7).

Figure 8 investigates, in more detail, the changes of sensing mechanism of ZnI2-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\(^{-1}\) in water from the original 0.4 g L\(^{-1}\).

The graph (Figure 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 vapor. 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). With this background, water vapor then appears as the only competing gas with formaldehyde.

As 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 Figure 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 0.04 g L$^{-1}$ with the 0.004 g L$^{-1}$ solution. If the water content was the main driving factor, then the 0.04 g L$^{-1}$ 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 vapor 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$^{-1}$ solution had a very fast recovery rate, suggesting that formaldehyde alone does not absorb firmly on to the nanotubes.

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 with that of the zinc iodide-filled DWNTs (Figure 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 the previous studies$^{[12]}$ 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 commercialization, more dedicated studies on stability and detection limit would be needed.

4. Conclusions

In conclusion, we have managed to tailor or tune the response of DWNTs toward 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, whereas the iodine enhances the selectivity toward 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.
Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon nanotubes, chemoresistive sensors, formaldehyde, metal encapsulation