Room temperature gas sensing properties of ultrathin carbon nanotube films by surfactant-free dip coating

Carlo Piloto¹, Francesca Mirri², E. Amram Bengio², Marco Notarianni^{1,3}, Bharati Gupta¹, Mahnaz Shafiei¹, Matteo Pasquali² and Nunzio Motta^{1*}

¹Institute for Future Environments and

School of Chemistry, Physics, and Mechanical Engineering,

Queensland University of Technology, Brisbane, QLD 4001, Australia

²Rice University, Chemical and Biomolecular Engineering, Houston, TX 77005,
United States

³Plasma-Therm LLC, 10050 16th St North, St. Petersburg, FL 33716 United States

*Corresponding author: n.motta@qut.edu.au

Abstract

Large-scale production of reliable carbon nanotubes (CNTs) based gas sensors involves the development of scalable and reliable processes for the fabrication of films with controlled morphology. Here, we report for the first time on highly scalable, ultrathin CNT films, to be employed as conductometric sensors for NO₂ and NH₃ detection at room temperature. The sensing films are produced by dip coating using dissolved CNTs in chlorosulfonic acid as a working solution. This surfactant-free approach does not require any post-treatment for the removal of dispersants or any CNTs functionalization, thus promising high quality CNTs for better sensitivity

and low production costs. The effect of CNT film thickness and defect density on the gas sensing properties has been investigated. Detection limits of 1 ppm for NO₂ and 7 ppm for NH₃ have been achieved at room temperature. The experimental results reveal that defect density and film thickness can be controlled to optimize the sensing response. Gas desorption has been accelerated by continuous *in-situ* UV irradiation.

Keywords

Carbon nanotubes, ultrathin films, gas sensors, surfactant-free dip coating, X-ray photoelectron microscopy, transmission electron microscopy

1. Introduction

Carbon nanotubes (CNTs) based sensors have been intensively studied in the past years due to their attractive properties including high sensitivity, room temperature operation, and very low detection limit[1-4]. Furthermore, CNT thin films can be potentially integrated into flexible, transparent, and low-cost electronic applications, thereby being attractive for portable and low-power devices [5]. Sensors based on single- or multi-walled CNTs (SWNTs or MWNTs) have proven to detect a wide

variety of polluting gases [6-12] and toxic volatile compounds, thus making CNTs highly suitable for environmental monitoring and medical applications [1, 13-19].

Several research groups reported an improvement in performance of CNT sensing devices by optimizing the film thickness and the network density. By producing a 200 nm SWCNTs film, Valentini et al. [20] achieved a remarkable conductometric signal variation of 6% for 100 ppb NO₂ at room temperature, though fast recovery was only achieved by heating the film at 165°C. Battie et al. [21] recently compared gas sensing performances of two SWCNTs films with different film thicknesses and network densities. Although the resistivity variation of the low density film at 200 ppm of NO₂ and NH₃ was sensibly higher, the higher density sample exhibited a lower detection limit (500ppb for NH₃ and 20ppb for NO₂) because of better signal/noise ratio. However, it is to be considered that here a different deposition technique (filtration vs spray coating) has been utilized. Sippel-Oakley et al. [22] fabricated a 7 nm Pd-functionalized SWCNTs thin film by filtration technique for hydrogen sensing achieving a relative resistance variation of 20% at 100 ppm and 30s recovery time.

Despite the intense study on the mechanism that regulates CNT chemiresistors, there is still a lack of consensus on how NO_x and NH₃ molecules interact with CNTs [23, 24]. The main sensing mechanisms that have been identified are the alteration of the Schottky barriers at the interface between CNTs/metal electrodes [25-27], the adsorption of target gas molecules at the interstitial sites in the CNT bundles [28-30] and direct charge transfer from the gas molecules on the SWNTs [31]. While experimental results confirmed that both Schottky barrier modulation and charge transfer between adsorbate molecules and CNTs play a crucial role in the sensing

mechanism [26, 28, 32], the scenario is more complex when considering networks of CNTs. Some investigations on sensors involving CNT networks suggested that molecular adsorption is the main detection mechanism [33], while other experiments confirmed the importance of the metal electrode/CNTs interface to determine the conduction change [23, 33]. By monitoring C1s XPS peak during NO₂ gas exposure, Larciprete et al. [27] excluded the possibility that any tube-adsorbate charge transfer takes place on the CNTs for temperatures above 200K. According to this result, the observed sensitivity of CNTs at room temperature is exclusively attributed to the interaction of NO₂ at the interface between CNTs and metal contacts.

Disagreement has also been found in theoretical calculations relative to the binding region between gas molecule and CNT networks. Some works suggest that, within a CNT network, NO₂ molecules bind preferably in the regions between CNTs rather than on a single CNT [32], while previous works propose the opposite scenario [34, 35].

A fabrication method that accurately controls CNT film morphology is therefore crucial for the development of reliable and high sensing performance chemiresistors. Moreover, this technique must be low-cost and scalable for high volume production in order to ease their integration into mass production devices [30, 36]. Many CNT film fabrication techniques are either not scalable or rely on the use of CNT dispersions obtained using surfactants [37-41], however these are known to be problematic because of the difficulty in removing the surfactants from the CNTs once the film is formed. Chlorosulfonic acid (CSA) has been shown to be the only true solvent for CNTs [42, 43] and has been successfully used to produce CNT surfactant-free thin films by scalable dip coating [44]. Moreover there is an interest in looking at the

effect of sonication on CNTs dispersed in solutions such as DMF or deionized water [45-47]. It has been proved that sonication influences CNTs properties changing their length and defect density, but there is a lack of understanding about the modification of the sensing properties.

Here, we report the fabrication of highly sensitive conductometric devices to NO₂ and NH₃ gases at room temperature using a sensing layer of dip coated CNT films made from CSA solutions. The proposed process is scalable and does not involve the use of expensive equipment which makes it an excellent candidate for mass production. Due to the reduced thickness of the films, a very low amount of material is needed to fabricate a sensor. Moreover the simplicity of the deposition technique ensures reproducibility of the sensors. In order to get a deeper understanding of the sensing mechanism, we developed ultrathin CNT films with different thicknesses and compared their sensing performances.

2. Experimental

CNT conductometric sensors were fabricated by depositing a CNT thin film on top of Pt- interdigitated electrode (IDTs) transducers with 250 μ m pitch. The CNT films were produced as described in previous work [44]. In brief, a solution made of CNTs (double wall nanotubes, purchased from Unidym) dissolved in CSA (Sigma Aldrich) was dip coated on a glass slide at a controlled speed and known solution concentration. Specifically, CNT films with thicknesses of 3, 5 and 10 nm were obtained by dip coating at a speed of 0.5, 5 and 10 mm/min, respectively with a 750 ppm by weight solution. Then, the CSA was removed from the films by coagulation in diethyl ether for 10 minutes, followed by a chloroform wash for 5 minutes. The CNT films were subsequently detached from the glass support by dipping them in

water and allowing the films to float on the water surface. The transducers were used to collect the films from the water bath and then air dried overnight. The size of the film was $14 \times 8 \text{ mm}^2$ in order to cover the Pt-interdigitated electrodes. The same process was repeated for a second set of films made with a CNT-CSA solution that was bath sonicated for 23 hours in order to study the effect of sonication on the CNT films properties and thus on their gas sensing performance. Since sonication is responsible for CNT shortening and therefore it decreases the solution viscosity, the films from the sonicated solution were dip coated at higher speeds of 2.3, 39 and 65 mm/min to obtain the same film thicknesses of 3, 5 and 10 nm at a solution concentration of 750 ppm in weight, respectively.

Material characterization was carried out using X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Raman.

The chemical composition of the samples was characterized by XPS using a non-monochromatic Mg K alpha (1253.6 eV) X-ray source (DAR 400, Omicron Nanotechnology), 300 W incident angle at 65 degree to the sample surface, with a 125 mm hemispherical electron energy analyser (Sphera II, 7 channels detector, Omicron Nanotechnology). Photoelectron data were collected at a take-off angle of 90 degree. The scans were carried out with 0.2 eV steps and 0.2 s dwell time. The pressure in the analysis chamber during XPS scans was kept below 5.0×10^{-9} mbar. TEM measurements of the average CNT diameter and number of walls were carried out using a JEOL 2100 FEG TEM at an accelerating voltage of 200 kV. Raman spectroscopy was carried out on the CNT films deposited on glass slides at 514 nm laser wavelength with a Renishaw inVia microscope. The objective was 50X

and the acquisition time was 10 s. SEM imaging was performed on the CNT films deposited on TEM grids to increase resolution [44] using a FEI Quanta 400 ESEM FEG microscope.

Response of the CNT film sensors to NO₂ and NH₃ gases was evaluated using a high precision gas testing system that includes a Teflon gas chamber (60 cc), 8 high precision mass flow controllers (MFC, MKS 1479A) to regulate the gas mixture, 8-channel MFC processing unit (MKS 647C), a picoammeter (Keithley 6487) and a climatic chamber (Steridium i170) to control the temperature. The measurements were performed at room temperature with a mixture of synthetic air and the target gases with different concentrations (max.12.2 ppm for NO₂ and 99 ppm for NH₃ balanced in synthetic air). The desired concentration of NO₂ and NH₃ gases was obtained by adjusting the respective flow rates via the MFCs, while maintaining a total constant flow rate of 200 SCCM (mL/min). The response upon gas exposure was evaluated by measuring the sensor resistance variation with an applied bias voltage of 10 mV. Continuous *in-situ* UV irradiation was used to accelerate the gas desorption. A quartz window in the chamber lid enabled the UV irradiation of the sample during the experiment. A UV lamp emitting at 395 nm was used with a maximum irradiating power of 50 W.

3. Results and discussion

3.1. Material characterization

In order to investigate the morphology of CNT thin film, SEM analysis was conducted on both sonicated and non-sonicated films. The morphology of the films appeared to be identical (Figure S1 in Supporting Info). To understand whether

sonication caused any changes in the CNTs network, measurements of the average CNT diameter and number of walls were carried out using TEM. As can be seen in Figure 1, CNTs aggregated to form nano-fibrils/bundles in the dry state. Only the individualized four-walled CNT can be included in the dataset, when in reality the image shows several other CNTs whose number of walls and diameter cannot be measured because they are not clearly distinguishable from one another. Furthermore, CNTs were mostly covered in amorphous carbon and H₂SO₄ residuals, complicating accurate wall-counting and diameter measurement. The measurements were made only on CNTs that were fully individualized, with a clearly defined number of walls on either side.

The standard errors of the measurements were evaluated using the bootstrap method [48], which has already been shown to give accurate estimates of standard errors for CNTs average length taken from multiple cryo-TEM images [49] (see Supporting Info, Figures S2-S5). A single-estimator bootstrap was first carried out by calculating the mean diameter $\langle d \rangle$ and mean number of walls $\langle w \rangle$ of each bootstrapped set.

Figure 1: TEM image of a four-walled CNT in a sonicated thin film.

A double-estimator bootstrap was also carried out by fitting a lognormal distribution to each bootstrapped set and obtaining estimates for the average mean diameter $\langle m_d \rangle$, variance in the diameter $\langle v_d \rangle$, mean number of walls $\langle m_w \rangle$ and variance in the number of walls $\langle v_w \rangle$ along with their respective standard errors.

Table 1: Summary of estimated parameters and standard errors from TEM measurements

Parameter	Non-sonicated CNTs	Sonicated CNTs
mean diameter $\langle d \rangle$	2.56 ± 0.12 nm	2.43 ± 0.09 nm

mean number of walls $\langle w \rangle$	2.45 ± 0.10	2.25 ± 0.09
average mean diameter $\langle m_d \rangle$	2.55 ± 0.12 nm	2.44 ± 0.09 nm
variance in the diameter $\langle v_d \rangle$	1.26 ± 0.32 nm	0.86 ± 0.16 nm
mean number of walls $\langle m_w \rangle$	2.46 ± 0.10	2.27 ± 0.10
variance in the number of walls $\langle v_w \rangle$	1.25 ± 0.21	1.10 ± 0.15

It is apparent that the only statistically significant difference between the sonicated and non-sonicated films is between the mean numbers of walls $\langle w \rangle$, as summarized in

Table 1. The parameters of the means and standard errors from the single- and double-estimator bootstrap measurements are in agreement, as expected (see Supporting Info, Figure S5-S6).

Theory suggests [50] that sonication might break the CNTs, in which case the outer walls would break first. The difference in mean number of walls $\langle w \rangle$ is just barely large enough to be statistically significant; this would suggest a breaking of the CNT outer walls and the reduction of the CNTs mean diameter. This lends credence to the theory that the CNT outer wall breaks first upon sonication, which in turn may increase the surface area.

XPS analysis was conducted for a better understanding on the evolution of the functional groups and the possible presence of structural defects upon sonication. XPS survey analysis shows the core level peak positions carbon (C 1s) and Oxygen (O 1s) are 284.5 and 532.1 eV respectively. High-resolution C1s spectra of the non-sonicated and sonicated 3 nm and 10 nm thick films are shown in Figure 2. The peak can be fitted by using four components, each representing a separate carbon bond: C-

C sp^2 at 284.5 eV, C-C sp^3 at 285.2 eV, C-OH at 286.1 eV and -COO at 289.1 eV [51-57]. The C-C sp^2 bond can be easily attributed to the graphitic structure of CNTs, while the C-C sp^3 bond can be assigned to links between CNTs in the bundles. The other two peaks are due to chemical bonds of carbon with hydroxyl and -COO species. It is evident in both samples that the fraction of C-C sp^3 bond decreases upon sonication, while that of the C-C sp^2 bond increases accordingly (Figure 2). This finding proves that sonication breaks the CNT outer walls as suggested by TEM and removes some spurious sp^3 carbon, thereby increasing the film cleanliness and the CNT film surface area. However, sonication did not significantly change the CNT structure as proved by Raman spectroscopy (Figure S7 in Supporting Info).

Figure 2: High resolution XPS spectra of C1s peak for the non-sonicated and sonicated samples.

Table 2: Summary of the XPS C1s analysis results that compares peak position and concentration before and after sonication.

bond		NS1	S1	NS3	S3
C=C sp2	peak	284.5	284.5	284.3	284.1
	% conc	22.0	32.6	15.1	53.1
C-C sp3	peak	285.2	285.2	285.0	285.1
	% conc	57.5	27.7	47.6	17.5
C-OH	peak	286.7	286.2	286.1	285.9
	% conc	13.3	32.6	28.4	14.2
-COO	peak	289.4	289.2	289.1	287.2
	% conc	7.2	7.1	9.0	15.2

3.2. Gas sensing performance

The electrical and sensing performances of the CNT films were investigated towards NO₂ and NH₃ gases balanced in synthetic air at room temperature. The response (R) was calculated according to the equation:

$$R\% = 100 \times \frac{(R_{air} - R_{gas})}{R_{air}} = 100 \times \frac{\Delta R}{R_{air}}$$

where R_{air} is the film resistance under synthetic air and R_{gas} is the film resistance upon exposure to the target gas.

Non sonicated samples

The CNT films exhibited a decrease in their resistivity upon exposure to NO₂. This was expected, as CNTs are p-type semiconductor in air and NO₂ is a hole donor gas. In addition, the CNT films produced in this work were expected to behave as p-type semiconductors due to the presence of acid residues from the fabrication process. As shown in Figure 3 (black curve), the non-sonicated 10 nm sensors exhibited 1% response to low concentration of NO₂ (3 ppm) at room temperature, but it did not

return to the original baseline. The irreversible gas desorption can be attributed to the strong binding energies between the CNT films and gas molecules. Theoretical studies [58, 59] showed that the slow desorption rate of NO₂ is due to the reaction of two NO₂ molecules into NO₃ triggered by CNTs. Chen et al. [60] previously reported that UV irradiation can accelerate molecular desorption from CNTs, where the desorption mechanism induced by UV light is attributed to plasmon excitation of CNTs. In this work, the sensors were irradiated by continuous UV light source emitting at 395 nm to overcome the long recovery. Figure 3 shows that the UV irradiation improved the recovery significantly and also enhanced the response. A possible explanation of the latter phenomenon is that UV light cleans the CNT surface making the CNT film more accessible for gas adsorption, as observed by Chen et al [60]. However a full understanding of this phenomenon is beyond the scope of this work. As the irradiation power increased, the response improved and the recovery time. As shown in Figure 4, the amount of response recovered after 30 minutes of air exposure increases linearly with increasing irradiating power.

Figure 3: Dynamic response of 10 nm thick CNTs sensor to 3 ppm NO₂ for different continuous UV irradiating power.

Figure 4: Amount of response recovered by 10 nm thick CNTs sensor after 30 minutes of air exposure as a function of UV irradiating power.

For the following experiments, all the gas sensors were tested with continuous UV irradiating power of 1400 mA, for a total power of 5 W.

Given that the gas sensing performance of CNT films can be enhanced by decreasing film thickness (i.e. CNT density) [21], we investigated three different film thicknesses, i.e. 3, 5 and 10 nm. Normalized dynamic response of these sensors towards 0.5, 1, 3 and 6 ppm NO₂ is shown in Figure 5. All three sensors showed a fast reaction upon exposure to NO₂ for 5 minutes and recovered their original value after approximately 50-60 minutes (Figure 5).

Appreciable variations were measured down to 1 ppm and even 0.5 ppm. The 5 nm thick sensor exhibited the fastest recovery and largest response as compared to the other sensors (Table 3 and Table 4).

The inset in Figure 5 highlights the linear response as a function of NO₂ concentrations.

Figure 5: Dynamic response of the non-sonicated sensors with different film thicknesses to NO₂ gas under continuous UV irradiation at 1400 mW. The inset shows the response as a function of NO₂ gas concentration.

Table 3: Response and recovery time of non-sonicated samples upon exposure to 1ppm NO₂.

	Film thickness		
(min)	3nm	5nm	10nm
$t_{response}$	4.7	4.8	4.9
$t_{recovery}$	63.1	53.9	64.9

Table 4: Response of different film thicknesses towards NO₂ at various concentrations.

NO ₂	Response %		
	Film thickness		
	3nm	5nm	10nm
0.5 ppm	0.04	0.33	0.06
1 ppm	0.56	1.23	0.86
3 ppm	3.28	5.7	2.29
6 ppm	4.28	7.6	3.11

Reducing film thickness from 10 nm to 5 nm in the gas sensor sensibly improves the device performance (Table 4). This is expected since by reducing film thickness the number of CNT pathways in the network is reduced, which in turns increases the impact of the pathways affected by gas adsorption to the overall path resistance of the CNT network. However, reducing the thickness even further to 3 nm causes a worse device performance. This phenomenon can be explained by the reduction of the number of CNTs in the sensor network, which results in the reduction of the number of available sites for gas adsorption. These results suggest that not only the CNT-CNT junctions [32] but the whole CNTs walls constitute area for gas adsorption. Hence, a tradeoff between reducing the film thickness and maintaining available sites for gas adsorption needs to be found in order to optimize the performances.

Sonicated samples

To further investigate the effect of CNT film morphology on gas sensing performance, we tested the sonicated sensors towards NO₂ and NH₃ at room temperature (Figure 6). After testing the sensors in different concentrations of NH₃, a

low detection limit of 7 ppm was observed. As expected NH_3 acts as an electron donor thus leading to an increase in p-type CNT film resistivity (Figure 6 c and d). The opposite behaviour of the sensor to NH_3 and NO_2 confirms the ability of the CNTs films to selectively detect NO_2 rather than NH_3 . An enhancement in the response of all three sensors to both NO_2 and NH_3 gases after sonication can be confirmed from Figure 7. It is evident that the response of the sensor after sonication is greatly enhanced for all three thicknesses. In particular, the 5 nm sensor was found to have almost double response (from 6 % to 11 %) after sonication.

Figure 6: Comparison between the dynamic response of non-sonicated and sonicated samples towards 3 ppm NO_2 (a-b) and 7 ppm NH_3 (c-d).

These improvements were expected as the TEM and XPS characterizations revealed that sonication increases the surface area available for gas adsorption by exposing both the inner wall and the broken outer wall. This conclusion is based on the qualitative assumption that the CNT outer wall, though broken, can still serve as a surface for the gas adsorption. Through sonication, we were able to increase the

available adsorption sites whilst keeping the film thickness unaltered [61, 62]. The recovery rate of sonicated samples was found to be faster than that of non-sonicated samples (5×10^{-3} vs 2.3×10^{-3}), but it is to be considered that the UV irradiation is hitting a larger exposed area.

The CNT sensors in this work demonstrated sensitivity to NO_2 and NH_3 , at concentrations as low as 1 ppm and 7 ppm, exhibiting (in the case of the 5 nm sensor) a resistivity variation of 1.2 % and 1 % respectively. Previous reports on sensors based on MWCNTs showed a detection limit of 0.1 ppm NO_2 [20] and 10 ppm NH_3 [63], respectively. While our NO_2 detection limit is lower compared to Valentini et al, it is to be considered that our fabrication method is far more simple and scalable.

Figure 7: Comparison between the response of non-sonicated and sonicated CNT sensors towards NO_2 and NH_3 as a function of film thickness.

4. Conclusions

In this work we show scalable fabrication of ultrathin CNT conductometric sensors operating at room temperature by surfactant-free process. Dip coating is a technique of choice for the fabrication of low cost and low power CNT sensor devices since it does not require dispersant removal that deteriorates CNT quality and increases production costs. We demonstrated that with this simple and scalable fabrication

technique it is possible to produce CNTs films with very high reproducibility and sensitivity. As the films are robust and thin, they can be integrated into flexible and transparent electronic applications. We found good sensing performances to concentrations as low as 1 ppm for NO₂ and 7 ppm for NH₃. The high sensitivity is attributed to the high density of CNTs deposited in an ultrathin film (~ 5 nm) by dip coating. Further improvements in the sensing performance were achieved by sonication of the CNTs film. XPS analysis highlighted the increase in surface area for gas interaction upon sonication. This new method suggests that CNT films can be used as sensing layer for the development of inexpensive, high performance room temperature gas sensors. Continuous *in-situ* UV irradiation was found not only to accelerate gas desorption but also to increase the gas response.

Acknowledgments

Research was supported by Air Force Office of Scientific Research (AFOSR) grants FA9550-12-1-0035 and FA9550-09-1-0590 (for F. M.). The authors acknowledge the support of the Australian Research Council (ARC) through the Discovery project DP130102120. The data reported in this paper were obtained at the *Central Analytical Research Facility* operated by the *Institute for Future Environments* (QUT). Access to CARF is supported by generous funding from the *Science and Engineering Faculty* (QUT).

References

- [1] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, *et al.*, "Nanotube molecular wires as chemical sensors," *Science*, vol. 287, pp. 622-625, // 2000.
- [2] M. F. L. De Volder, S. H. Tawfick, R. H. Baughman, and A. J. Hart, "Carbon Nanotubes: Present and Future Commercial Applications," *Science*, vol. 339, pp. 535-539, February 1, 2013 2013.
- [3] S. Basu and P. Bhattacharyya, "Recent developments on graphene and graphene oxide based solid state gas sensors," *Sensors and Actuators, B: Chemical*, vol. 173, pp. 1-21, // 2012.
- [4] T. Ueda, M. Bhuiyan, H. Norimatsu, S. Katsuki, T. Ikegami, and F. Mitsugi, "Development of carbon nanotube-based gas sensors for NO_x gas detection working at low temperature," *Physica E: Low-dimensional Systems and Nanostructures*, vol. 40, pp. 2272-2277, 2008.
- [5] Y. I. Song, C.-M. Yang, D. Y. Kim, H. Kanoh, and K. Kaneko, "Flexible transparent conducting single-wall carbon nanotube film with network bridging method," *Journal of Colloid and Interface Science*, vol. 318, pp. 365-371, 2/15/ 2008.
- [6] S. M. Seo, T. J. Kang, J. H. Cheon, Y. H. Kim, and Y. J. Park, "Facile and scalable fabrication of chemiresistive sensor array for hydrogen detection based on gold-nanoparticle decorated SWCNT network," *Sensors and Actuators B: Chemical*, vol. 204, pp. 716-722, 12/1/ 2014.
- [7] J.-J. Adjizian, R. Leghrib, A. A. Koos, I. Suarez-Martinez, A. Crossley, P. Wagner, *et al.*, "Boron- and nitrogen-doped multi-wall carbon nanotubes for gas detection," *Carbon*, vol. 66, pp. 662-673, 1// 2014.
- [8] A. Abdelhalim, A. Abdellah, G. Scarpa, and P. Lugli, "Metallic nanoparticles functionalizing carbon nanotube networks for gas sensing applications," *Nanotechnology*, vol. 25, p. 055208, 2014.
- [9] A. Abdellah, A. Abdelhalim, M. Horn, G. Scarpa, and P. Lugli, "Scalable Spray Deposition Process for High-Performance Carbon Nanotube Gas Sensors," *Nanotechnology, IEEE Transactions on*, vol. 12, pp. 174-181, 2013.
- [10] M. Penza, R. Rossi, M. Alvisi, D. Suriano, and E. Serra, "Pt-modified carbon nanotube networked layers for enhanced gas microsensors," *Thin Solid Films*, vol. 520, pp. 959-965, 2011.
- [11] S. Mubeen, J. H. Lim, A. Srirangarajan, A. Mulchandani, M. A. Deshusses, and N. V. Myung, "Gas Sensing Mechanism of Gold Nanoparticles Decorated Single-Walled Carbon Nanotubes," *Electroanalysis*, vol. 23, pp. 2687-2692, 2011.

- [12] E. Şennik, Z. Çolak, N. Kiliç, and Z. Z. Öztürk, "Synthesis of highly-ordered TiO₂ nanotubes for a hydrogen sensor," *International Journal of Hydrogen Energy*, vol. 35, pp. 4420-4427, 2010.
- [13] P. Collins, K. Bradley, M. Ishigami, and A. Zettl, "Extreme oxygen sensitivity of electronic properties of carbon nanotubes," *Science*, vol. 287, p. 1801, 2000.
- [14] P. Bondavalli, P. Legagneux, and D. Pribat, "Carbon nanotubes based transistors as gas sensors: State of the art and critical review," *Sensors and Actuators, B: Chemical*, vol. 140, pp. 304-318, // 2009.
- [15] K. Bradley, J.-C. P. Gabriel, M. Briman, A. Star, and G. Grüner, "Charge Transfer from Ammonia Physisorbed on Nanotubes," *Physical Review Letters*, vol. 91, p. 218301, 11/17/ 2003.
- [16] S. Kim, H. R. Lee, Y. J. Yun, S. Ji, K. Yoo, W. S. Yun, *et al.*, "Effects of polymer coating on the adsorption of gas molecules on carbon nanotube networks," *Applied Physics Letters*, vol. 91, pp. -, 2007.
- [17] I. Sayago, E. Terrado, M. Aleixandre, M. C. Horrillo, M. J. Fernández, J. Lozano, *et al.*, "Novel selective sensors based on carbon nanotube films for hydrogen detection," *Sensors and Actuators B: Chemical*, vol. 122, pp. 75-80, 3/8/ 2007.
- [18] H. Dai, "Carbon nanotubes: opportunities and challenges," *Surface Science*, vol. 500, pp. 218-241, 3/10/ 2002.
- [19] S. N. Kim, J. F. Rusling, and F. Papadimitrakopoulos, "Carbon nanotubes for electronic and electrochemical detection of biomolecules," *Advanced Materials*, vol. 19, pp. 3214-3228, Oct 2007.
- [20] L. Valentini, C. Cantalini, I. Armentano, J. M. Kenny, L. Lozzi, and S. Santucci, "Highly sensitive and selective sensors based on carbon nanotubes thin films for molecular detection," *Diamond and Related Materials*, vol. 13, pp. 1301-1305, 4// 2004.
- [21] Y. Battie, L. Gorintin, O. Ducloux, P. Thobois, P. Bondavalli, G. Feugnet, *et al.*, "Thickness dependent sensing mechanism in sorted semi-conducting single walled nanotube based sensors," *Analyst*, vol. 137, pp. 2151-2157, 2012.
- [22] S.-O. Jennifer, W. Hung-Ta, S. K. Byoung, W. Zhuangchun, R. Fan, G. R. Andrew, *et al.*, "Carbon nanotube films for room temperature hydrogen sensing," *Nanotechnology*, vol. 16, p. 2218, 2005.
- [23] A. Boyd, I. Dube, G. Fedorov, M. Paranjape, and P. Barbara, "Gas sensing mechanism of carbon nanotubes: From single tubes to high-density networks," *Carbon*, vol. 69, pp. 417-423, 4// 2014.
- [24] I. Heller, A. M. Janssens, J. Männik, E. D. Minot, S. G. Lemay, and C. Dekker, "Identifying the mechanism of biosensing with carbon nanotube transistors," *Nano Letters*, vol. 8, pp. 591-595, 2008.
- [25] N. Iqbal, A. Afzal, N. Cioffi, L. Sabbatini, and L. Torsi, "NO_x sensing one- and two-dimensional carbon nanostructures and nanohybrids: Progress and

- perspectives," *Sensors and Actuators B: Chemical*, vol. 181, pp. 9-21, 5// 2013.
- [26] J. Zhang, A. Boyd, A. Tselev, M. Paranjape, and P. Barbara, "Mechanism of NO₂ detection in carbon nanotube field effect transistor chemical sensors," *Applied Physics Letters*, vol. 88, p. 123112, 2006.
 - [27] R. Larciprete, L. Petaccia, S. Lizzit, and A. Goldoni, "The role of metal contact in the sensitivity of single-walled carbon nanotubes to NO₂," *The Journal of Physical Chemistry C*, vol. 111, pp. 12169-12174, 2007.
 - [28] T. Helbling, R. Pohle, L. Durrer, C. Stampfer, C. Roman, A. Jungen, *et al.*, "Sensing NO₂ with individual suspended single-walled carbon nanotubes," *Sensors and Actuators B: Chemical*, vol. 132, pp. 491-497, 2008.
 - [29] T. Helbling, C. Hierold, L. Durrer, C. Roman, R. Pohle, and M. Fleischer, "Suspended and non-suspended carbon nanotube transistors for NO₂ sensing—A qualitative comparison," *physica status solidi (b)*, vol. 245, pp. 2326-2330, 2008.
 - [30] A. Jungen, C. Stampfer, L. Durrer, T. Helbling, and C. Hierold, "Amorphous carbon contamination monitoring and process optimization for single-walled carbon nanotube integration," *Nanotechnology*, vol. 18, p. 075603, 2007.
 - [31] O. K. Varghese, P. D. Kichambre, D. Gong, K. G. Ong, E. C. Dickey, and C. A. Grimes, "Gas sensing characteristics of multi-wall carbon nanotubes," *Sensors and Actuators B: Chemical*, vol. 81, pp. 32-41, 12/15/ 2001.
 - [32] N. Peng, Q. Zhang, C. L. Chow, O. K. Tan, and N. Marzari, "Sensing mechanisms for carbon nanotube based NH₃ gas detection," *Nano letters*, vol. 9, pp. 1626-1630, 2009.
 - [33] Y. Battie, O. Ducloux, P. Thobois, N. Dorval, J. S. Lauret, B. Attal-Trétout, *et al.*, "Gas sensors based on thick films of semi-conducting single walled carbon nanotubes," *Carbon*, vol. 49, pp. 3544-3552, 2011.
 - [34] H. Chang, J. D. Lee, S. M. Lee, and Y. H. Lee, "Adsorption of NH₃ and NO₂ molecules on carbon nanotubes," *Applied Physics Letters*, vol. 79, pp. 3863-3865, 2001.
 - [35] J. Zhao, A. Buldum, J. Han, and J. P. Lu, "Gas molecule adsorption in carbon nanotubes and nanotube bundles," *Nanotechnology*, vol. 13, p. 195, 2002.
 - [36] Q. Zhang, J.-Q. Huang, M.-Q. Zhao, W.-Z. Qian, and F. Wei, "Carbon Nanotube Mass Production: Principles and Processes," *ChemSusChem*, vol. 4, pp. 864-889, 2011.
 - [37] M. Kaempgen, G. S. Duesberg, and S. Roth, "Transparent carbon nanotube coatings," *Applied Surface Science*, vol. 252, pp. 425-429, 10/15/ 2005.
 - [38] J. S. Moon, J. H. Park, T. Y. Lee, Y. W. Kim, J. B. Yoo, C. Y. Park, *et al.*, "Transparent conductive film based on carbon nanotubes and PEDOT composites," *Diamond and Related Materials*, vol. 14, pp. 1882-1887, 11// 2005.

- [39] K. Parikh, K. Cattanach, R. Rao, D.-S. Suh, A. Wu, and S. K. Manohar, "Flexible vapour sensors using single walled carbon nanotubes," *Sensors and Actuators B: Chemical*, vol. 113, pp. 55-63, 1/17/ 2006.
- [40] K. A. Jose, P. Biju, W. Ashwin, K. V. Vijay, and C. C. Reddy, "A compact wireless gas sensor using a carbon nanotube/PMMA thin film chemiresistor," *Smart Materials and Structures*, vol. 13, p. 1045, 2004.
- [41] Z. Liu, H. Li, Z. Qiu, S. L. Zhang, and Z. B. Zhang, "SMALL-Hysteresis Thin-Film Transistors Achieved by Facile Dip-Coating of Nanotube/Polymer Composite," *Advanced Materials*, vol. 24, pp. 3633-3638, 2012.
- [42] A. N. G. Parra-Vasquez, N. Behabtu, M. J. Green, C. L. Pint, C. C. Young, J. Schmidt, *et al.*, "Spontaneous Dissolution of Ultralong Single- and Multiwalled Carbon Nanotubes," *ACS Nano*, vol. 4, pp. 3969-3978, 2010/07/27 2010.
- [43] V. A. Davis, A. N. G. Parra-Vasquez, M. J. Green, P. K. Rai, N. Behabtu, V. Prieto, *et al.*, "True solutions of single-walled carbon nanotubes for assembly into macroscopic materials," *Nat Nano*, vol. 4, pp. 830-834, 12//print 2009.
- [44] F. Mirri, A. W. K. Ma, T. T. Hsu, N. Behabtu, S. L. Eichmann, C. C. Young, *et al.*, "High-performance carbon nanotube transparent conductive films by scalable dip coating," *ACS Nano*, vol. 6, pp. 9737-9744, 2012.
- [45] K. L. Lu, R. M. Lago, Y. K. Chen, M. L. H. Green, P. J. F. Harris, and S. C. Tsang, "Mechanical damage of carbon nanotubes by ultrasound," *Carbon*, vol. 34, pp. 814-816, // 1996.
- [46] D.-Q. Yang, J.-F. Rochette, and E. Sacher, "Functionalization of Multiwalled Carbon Nanotubes by Mild Aqueous Sonication," *The Journal of Physical Chemistry B*, vol. 109, pp. 7788-7794, 2005/04/01 2005.
- [47] W. Huang, Y. Lin, S. Taylor, J. Gaillard, A. M. Rao, and Y.-P. Sun, "Sonication-assisted functionalization and solubilization of carbon nanotubes," *Nano Letters*, vol. 2, pp. 231-234, 2002.
- [48] B. Efron, "Bootstrap methods: another look at the jackknife," *The annals of Statistics*, pp. 1-26, 1979.
- [49] E. A. Bengio, D. E. Tsentalovich, N. Behabtu, O. Kleinerman, E. Kesselman, J. Schmidt, *et al.*, "Statistical length measurement method by direct imaging of carbon nanotubes," *ACS applied materials & interfaces*, vol. 6, pp. 6139-6146, 2014.
- [50] Y. Miyata, M. Suzuki, M. Fujihara, Y. Asada, R. Kitaura, and H. Shinohara, "Solution-Phase Extraction of Ultrathin Inner Shells from Double-Wall Carbon Nanotubes," *ACS Nano*, vol. 4, pp. 5807-5812, 2010/10/26 2010.
- [51] H. Hiura, T. W. Ebbesen, and K. Tanigaki, "Opening and purification of carbon nanotubes in high yields," *Advanced Materials*, vol. 7, pp. 275-276, 1995.
- [52] A. Goldoni, R. Larciprete, L. Gregoratti, B. Kaulich, M. Kiskinova, Y. Zhang, *et al.*, "X-ray photoelectron microscopy of the C1s core level of free-standing

- single-wall carbon nanotube bundles," *Applied Physics Letters*, vol. 80, pp. 2165-2167, 2002.
- [53] P. X. Hou, S. Bai, Q. H. Yang, C. Liu, and H. M. Cheng, "Multi-step purification of carbon nanotubes," *Carbon*, vol. 40, pp. 81-85, 2002.
 - [54] W. H. Lee, S. J. Kim, W. J. Lee, J. G. Lee, R. C. Haddon, and P. J. Reucroft, "X-ray photoelectron spectroscopic studies of surface modified single-walled carbon nanotube material," *Applied Surface Science*, vol. 181, pp. 121-127, 2001.
 - [55] S. E. Baker, W. Cai, T. L. Lasseter, K. P. Weidkamp, and R. J. Hamers, "Covalently Bonded Adducts of Deoxyribonucleic Acid (DNA) Oligonucleotides with Single-Wall Carbon Nanotubes: Synthesis and Hybridization," *Nano Letters*, vol. 2, pp. 1413-1417, 2002.
 - [56] K. A. Wepasnick, B. A. Smith, J. L. Bitter, and D. H. Fairbrother, "Chemical and structural characterization of carbon nanotube surfaces," *Analytical and bioanalytical chemistry*, vol. 396, pp. 1003-1014, 2010.
 - [57] T. Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin, and N. Brown, "High resolution XPS characterization of chemical functionalised MWCNTs and SWCNTs," *Carbon*, vol. 43, pp. 153-161, 2005.
 - [58] S. Peng, K. Cho, P. Qi, and H. Dai, "Ab initio study of CNT NO₂ gas sensor," *Chemical Physics Letters*, vol. 387, pp. 271-276, 4/1/ 2004.
 - [59] E. Llobet, "Gas sensors using carbon nanomaterials: A review," *Sensors and Actuators, B: Chemical*, vol. 179, pp. 32-45, // 2013.
 - [60] G. Chen, T. M. Paronyan, E. M. Pigos, and A. R. Harutyunyan, "Enhanced gas sensing in pristine carbon nanotubes under continuous ultraviolet light illumination," *Scientific reports*, vol. 2, 2012.
 - [61] F. Léonard and J. Tersoff, "Role of Fermi-Level Pinning in Nanotube Schottky Diodes," *Physical Review Letters*, vol. 84, pp. 4693-4696, 05/15/ 2000.
 - [62] F. Léonard and J. Tersoff, "Novel Length Scales in Nanotube Devices," *Physical Review Letters*, vol. 83, pp. 5174-5177, 12/13/ 1999.
 - [63] S. Junya, Z. Guangbin, and H. Masanori, "Fabrication of a carbon nanotube-based gas sensor using dielectrophoresis and its application for ammonia detection by impedance spectroscopy," *Journal of Physics D: Applied Physics*, vol. 36, p. L109, 2003.