Customizing hydrothermal properties of inkjet printed sensitive films by functionalization of carbon nanotubes

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Abstract
Multiwalled carbon nanotubes (MWCNTs) are attractive materials for realizing sensors, owing to their high aspect ratio associated with excellent mechanical, electronic, and thermal properties. Moreover, their sensing properties can be tuned by introducing functional groups on their framework and adjusting the processing conditions. In this paper, we investigate the potential of functionalized CNTs for humidity and temperature sensing by optimization of the functionalization, the processing conditions and the printing conditions. The morphology of the differently functionalized MWCNTs is investigated by infrared spectroscopy (IR), scanning electron microscopy, thermogravimetry (TG) and TG-coupled mass-spectrometric studies. Using the functionalized MWCNTs, films were fabricated with different numbers of layers (4, 6, 8, 10 layers) via inkjet printing on a flexible polyimide substrate containing an interdigital microelectrode. The influence of hydrothermal effects was investigated. The sensitivity to humidity is higher for films prepared with MWCNTs functionalized with a high sonication amplitude and a bigger number of layers due to enhancements of hydrophilicity and water mobility. A higher sensitivity to temperature is achieved by a low sonication amplitude and a small number of layers. For the encapsulation of the temperature sensor against humidity, a Bectron layer is proposed, which reduces also the hysteresis effect. This study demonstrates the efficiency of carboxylic functionalized MWCNTs deposit by inkjet printing for realization of sensitive and cost-effective humidity and temperature sensors. It provides a real example for the interesting contribution of functionalization procedures to the sensing properties of MWCNTs films.

Keywords: functionalized CNTs, inkjet printing, temperature and humidity sensing

(Some figures may appear in colour only in the online journal)

1. Introduction
Humidity and temperature sensors are common use devices as they have great importance in diverse fields, such as medical applications for human comfort and industrial applications for monitoring devices in automobile industry or in agriculture for soil water content determination, etc [1]. To this aim,
different kinds of sensing materials have been used such as semiconducting materials [2], polymers [3], porous silicones [4, 5] and porous ceramics [6, 7].

However, sensors based on these materials suffer from low sensitivity, high cost, low stability, and reliability, which confines the development of humidity and temperature sensors in practical applications [8–10].

In order to overcome these limitations, the demand for novel smart materials has been increased using different nanomaterials e.g. nanoparticles, nanowires and carbon nanomaterials [7–13]. Among those materials, carbon nanomaterials including graphene and carbon nanotubes (CNTs) have attracted much attention due to their low-cost, large-scale synthesis, good electronic and mechanical properties [14, 15]. CNTs are very promising candidates for both temperature and humidity sensing since they are well known to have hydrothermal-dependent response of the electrical resistance [16, 17]. In fact, Li et al [18] found that the doping multiwalled carbon nanotubes (MWCNTs) in graphene oxide (GO) humidity sensor leads to the enhancement by thirteen times more than that of the sensor with GO film. This later demonstrates the important role of CNT for sensing application. However, the difficulty that hinder the use of CNTs for sensing applications is that this one-dimensional structure tends to form agglomerations when it is dispersed in common solvents caused by their large surface area and van der Walls attractive forces [1]. Furthermore, CNTs are hydrophobic in nature making the dispersibility very difficult in solution [19]. Given to this effect, the sensitivity to environmental change will be less. In order to circumvent this problem, several routes have been proposed to enhance the CNTs distribution and compatibility to other solvent using chemical treatments (covalent functionalization) or physical treatments. However, physical treatments introduce non-stable functionalization of the CNTs and weaker dispersibility with solvents comparing to the chemical treatments. Therefore, covalent functionalization is considered as a prominent method to enhance the quality of MWCNTs dispersions.

There are many approaches for chemical treatment [20, 21]. Among all, acid treatment using nitric acid (HNO₃) or a mixture of (HNO₃) and sulfuric acid (H₂SO₄) are the most reported in literature, especially for temperature [22] and humidity sensing applications [23]. Owing to their efficiency to enhance the nanotube dispersibility in solution that enables controlled deposition of thin films. Jung et al [24] reported about humidity sensors made of spin-capable multi-walled carbon. They found that the performance of the sensor such as the sensitivity and response time of the sensor is boosted by acid treatment.

In addition, Turkani et al [25] demonstrates that the presence of hydroxyl and carboxyl groups due to carboxylic functionalization of MWCNTs leads to increase the affinity towards water molecules. The improved interaction between functionalized MWCNTs and water molecules will contribute to increase the number of electrons transferred leading to a much higher resistance change.

Not only acid treatments allow to introduce the carboxyl, hydroxyls functional groups on the CNT surface, which make the surface more hydrophilic, but it leads also to functionalize the defects and the ends of the CNTs [26]. However, excessive acid treatment can result the damage of the CNT structure by shortening the CNTs and introduction of defects [27]. Therefore, the selection of the most suitable methodologies that combine a high degree of functionalization with proper preservation of CNTs structure is of high relevance for an adequate and high sensing performance.

However, the efficiency of the chemical treatment on the distribution of MWCNTs in solution arises, when it is accompanied with the suitable mixing approach. Several approaches have been adopted in order to achieve the homogenous and stable separation of CNTs in the solvent medium. Methods like shear mixing, mechanical stirring and sonication most reported in previous works, which will impart physical shear stress to break down CNT bundles and to disperse CNTs in the solvent [28–32].

Furthermore, during the fabrication of CNTs based temperature and humidity sensor, the chosen deposition technique plays a deterministic role on the quality of the deposit film as well on the sensing performance. Different techniques have been adopted in previous works such as mold casting, stencil printing, screen printing and drop casting etc. Among those methods, inkjet printing in one of the prominent approach, which utilizes in many flexible electronic applications due to its high degree of customization, processing in ambient condition, low amount of waste and non-impact nature. Inkjet printing of CNTs in form or composites or dispersion was realized previously by different research groups [28–32]. To form stable dispersions, MWCNTs have to be well dispersed in the ink. The main challenge here as was mentioned previously are van der Waals forces and high aspect ratio of the tubes, which lead to high inter-tube interaction and nanotubes bundling [33]. One of the strategies for preventing agglomeration is adding surfactant [28]. Additionally, often centrifugation and filtration required to reduce the number of aggregates and prevent clogging of the nozzles [28, 31]. Thanks to the chemical functionalization of MWCNTs, in this research it was possible to print dispersion of MWCNTs as prepared. Another parameter is the size of the orifice of the inkjet nozzles, which dictates the size of the dispersed in the ink particles. Depend on the printhead, this size can be varied. For reliable printing, Dimatix recommends using particles that diameter does not exceed 1/200 of the nozzle orifice [34]. Compare to drop casting or dispenser printing, inkjet is more precise in dosage of the CNTs dispersion. The nominal size of the drop can reach up to 10 pl. Because of the smallest drops, better distribution of CNTs can be achieved in the printed area. The good distribution of the CNTs and the precision of the CNTs dosage will improve repeatability of the printed layers, which is beneficial for repeatability of the sensor characteristics. Furthermore, advances in the chemical functionalization of CNTs make it possible to obtain a stable dispersion of CNTs for deposition by inkjet printing. Size of the tubes, their concentration and quality of dispersion are major importance for reliable printing. This study shows that the accumulation of nanotube at the edge of printed droplet needs to be avoided in order to
reduce the resistance and increase the humidity sensitivity of the MWCNTs films.

In this work, based on all these studies, we demonstrate the efficiency of carboxylic functionalization of CNT deposit via inkjet printing method to achieve highly sensitive, low concentration of CNTs and cost-effective humidity and temperature sensors with good reproducibility. Chemical treatment of CNTs based on carboxylic functionalization groups is proposed and performed under different process conditions. The respective dispersions are printed on a Kapton HN-polyimide substrate via inkjet printing with different number of layers. Scanning electron microscopy (SEM) characterization was carried out to get information about the impact of various treatment conditions on the CNTs distribution. In addition, microscopic and topographic measurements were performed for the different printed sensors. Finally, the printed films were investigated under humidity and temperature changes to select the suitable dispersion for each application. The main sensors characteristics such as sensitivity, hysteresis and stability were addressed and evaluated.

2. Materials and methods

2.1. Materials

The MWCNTs (purity 95% +%, average length of about 1–2 µm and average diameter of 20–40 nm) used in this study were purchased from IoLiTec Ionic Liquids Technologies GmbH. For the functionalization of the MWCNTs chemical oxidation processes were applied using ultrasonication methodology [35, 36].

2.2. Functionalization of MWCNTs by ultrasonication

To 300 mg of MWCNTs, 56 ml of a concentrated H2SO4/HNO3 mixture (ratio 3:1, v/v) were added in a single portion. The mixture was then sonicated with an ultrasonic horn (Bandelin sonopuls ultrasonic homogenizer SH 70/213 G; 200 W; 20 kHz) at ambient temperature for 30 min by varying amplitudes (20% or 40%), which corresponding 23 kJ and 33 kJ respectively. After the sonication the acidic MWCNTs mixture was poured into 100 ml of distilled water and subsequently centrifugaled at 25 °C for 40 min at 9500 rpm. The separated MWCNTs were treated with 30 ml of distilled water and sonicated for 10 min in an ultrasonic bath. After addition of 100 ml of diethyl ether to the dispersion, the functionalized MWCNTs were separated by centrifugation (10 °C, 9500 rpm, 50 min). The washing process was repeated until the pH of the aqueous supernatant solution was neutral. After that, the MWCNTs were dried in vacuum (10 mbar) at 110 °C. The samples are denoted as f-MWCNTs-1 (20% amplitude) or f-MWCNTs-2(40% amplitude).

2.3. Sensor preparation by inkjet printing

Using two different prepared functionalized MWCNTs (f-MWCNTs-1, f-MWCNTs-2), two dispersions were prepared by dispersing 0.05 wt% of MWCNTs into 20 ml of isopropanol solvent. Here, low CNTs concentration is chosen to avoid the formation of agglomerations which leads to nozzle clogging in inkjet printing. Furthermore, an organic solvent having high polarity was used to maintain good dispersibility and stability of the dispersion over time as demonstrated in our previous study [26]. In fact, functionalized CNTs has more affinity with highly polar organic solvents. In order to promote better distribution of the CNTs within the solvent, the solution was sonicated and mixed using a horn sonicator (Bandelin GM 3200, sonication temperature: 25 °C, sonication power: 30%) for 120 min (15.612 kJ) as shown in figure 1(a).

Inkjet printed sensors were fabricated using laboratory piezoelectric printer (Dimatix DMP 2831, Fujifilm, USA). The printer was equipped with a 10 pl print head consisting of 16 nozzles with a diameter of 21.5 µm. A single sensor layout consists of eight-finger interdigitated electrode with finger width of 100 µm, space between fingers 400 µm and sensing area of 4.0 × 3.7 mm² as illustrated in figure 1(b). The fabrication of sensors was performed by following these steps; deposition of silver electrodes, thermal sintering, deposition of CNTs dispersion and curing. Commercially available silver ink UTDAgIJ1 (UT Dots, Inc., USA) based on hydrocarbons has been used for inkjet printing of electrodes. To identify the ‘optimal’ drop space for the printing of silver electrodes, the lines with drop spaces from 5 to 140 µm were printed. The width of the lines in the digital file was 1 pixel. If the drop space was too high, the printed drops of silver ink were not in contact, and the line was not formed. At lower drop spaces, the higher spreading of the ink occurs. The optimal was considered drop space, which provided the closed printed line with straight borders and without spreading. The temperature of the substrate was kept at 40 °C, the actual printhead temperature was 36 °C. The optimal drop space was found as 35 µm. After deposition, the substrate was placed in oven for 20 min at 160 °C. Preliminary tests on PET showed deformation after thermal sintering, which led to loss of registration accuracy between deposited CNTs and array of electrodes. Therefore, in this work Kapton was chosen as a substrate due to its dimensional stability during sintering.

Two dispersions of CNTs in isopropanol f-MWCNTs-1 and f-MWCNTs-2 were used for printing. Each CNT-dispersion was filled in inert cartridge and immediately printed with 10 µm drop space on top of silver electrodes. Up to 10 overprints of CNT-dispersion were deposited. To ensure the removal of isopropanol residuals, the printed sensors were placed in an oven for 20 min at 80 °C. As the CNTs concentration in dispersion is very low, therefore to achieve measurable resistance of the sensor (in a range of MΩ), it was required to print multiple overprints of CNTs. The number of overprints can be minimized by reducing the drop space. By reducing the drop space, the amount of ink in one overprint was increased due to a higher amount of drops on the unit area. To facilitate the drying of the isopropanol, the substrate temperature was kept at 45 °C. The temperature of the cartridge was set at 35 °C. The jetted drops had a long tail. The diameter of single drop was measured on the substrate after...
drying. For the mentioned below temperature settings, the diameter of a dried single drop was in a range of 60 μm. In this research, 10 μm drop space for the deposition of CNTs dispersion was used. Very low drop space (minimum possible for Dimatix DMP 2831 is 5 μm) led uncontrollable spreading of the ink. Drop space of 10 μm was chosen for sensor printing because this value was high enough to prevent the uncontrollable spreading of the ink and low enough to keep the number of overprints between 4 and 10 to achieve a desirable range of sensor resistance MΩ. Both dispersions were good printable, no nozzle clogging occurred during sensors printing. In addition, the CNT-dispersion was printed with different amount of overprints on top of a glass slide for further surface profile characterizations.

3. Characterizations

3.1. Material characterization

Infrared spectroscopy (IR) was carried out to verify the chemical modification of the CNTs. Thermogravimetry (TG) and TG-coupled mass-spectrometric experiments (TG-MS) were employed to provide a quantitative identification of surface functional groups. In order to investigate the effect of chemical functionalization regarding to debundling of CNTs, SEM was used. The FT-IR spectra were recorded with a Thermo Nicolet IR 200 instrument using KBr pellets. SEM measurements were performed with a Philips NanoNova-SEM. The samples for SEM measurements were prepared by sonication of 1 mg of the MWCNTs in 6.40 ml of isopropanol in an ultrasonic bath for 10 min. Subsequently, one or two drops of the resulting MWCNTs were put onto a carbon film supported by 300 mesh copper grids and allowed to evaporate. The TG and TG-MS experiments were carried out with a Mettler Toledo TGA/DSC1 1600 system with a MX1 balance coupled with Pfeifer Vacuum MS Thermostar GSD 301 T2 mass spectrometer.

3.2. Printed layers characterization

Optical analysis of the printed layers was investigated by evaluating micrographs, taken with a light microscope (Leica DM4000). The electrical resistance of printed sensors was determined with a portable multimeter (VC 840). Here, the resistance measurement was conducted on 6–11 samples to determine their reproducibility and the average resistance value. The surface of f-MWCNTs-1 was characterized with a surface profiler (Veeco Dektak 150).

3.3. Sensors characterization

In order to study the humidity response of functionalized MWCNTs films, each sample was attached with two wires...
and connected to Keithley 2602A sourcemeter connected to a host computer. $I$–$V$ characteristics were measured by applying a DC voltage from 0 to 1 V. The electrical measurements were carried out by placing the samples in a glass solution bottle corresponding to a given defined relative humidity (RH) for fixed time until the RH of the salt solution get stabilized. The controlled humidity environments were achieved using saturated salt solutions as shown in figure 2, where each solution has specific RH; LiCl for 11% RH, MgCl$_2$ for 32% RH, Mg(NO$_3$)$_2$ for 54% RH, NaCl for 75% RH, KCl for 85% RH and K$_2$SO$_4$ for 97% RH at room temperature (23°C). The variations in the resistance with respect to the increase and decrease in the humidity were calculated from the $I$–$V$ curve and plotted to the hysteresis graph of the sensing material under adsorption and desorption.

To investigate the temperature dependency of resistance for the sensing material, the samples were subjected to a slow thermal cycle load; heating from 10°C to 80°C with a step of 10°C after each 20 min using an electronically regulated oven. The measurements were carried out at fixed humidity by keeping the samples in the glass bottle containing silica gel granules to eliminate the impact of humidity, when evaluating the temperature sensing properties of the composite material.

In temperature measurement, the relative resistance are calculated as follows:

$$\Delta R_t = \left(\frac{R_t - R_{0t}}{R_{0t}}\right) \times 100,$$

where $R_t$ is resistance at temperature $t$, $R_{0t}$ is initial resistance at 10°C.

In humidity measurement, the relative resistance are calculated as follows:

$$\Delta R_h = \left(\frac{R_h - R_{0h}}{R_{0h}}\right) \times 100,$$

where $R_h$ is resistance at relative humidity %RH, $R_{0h}$ is initial resistance at 11% RH.

4. Results and discussions

4.1. Chemical characterization of functionalized MWCNTs

The IR spectra of the pristine MWCNTs, f-MWCNTs-1, and f-MWCNTs-2 are depicted in figure 3 showing the vibrational bands at 1195 and 1567 cm$^{-1}$, which are characteristic for MWCNTs [37]. The first one is assigned to the C–C vibration of the MWCNTs, while the second one can be ascribed to the vibration of the carbon skeleton of the CNTs [37, 38]. The IR spectra of the functionalized MWCNTs show an additional band at 1706 cm$^{-1}$, which is characteristic for the $\nu_{CO}$ stretching vibration of the CO$_2$H group. The presence of a broad vibrational band at 3402 cm$^{-1}$ is representative for a
The range of 150 °C of the adsorbed water on the surface [48x251].

In argon atmosphere pristine MWCNTs start to decompose at 658 °C (figure 5) and thus at much higher temperature compared to f-MWCNTs-1 and f-MWCNTs-2. The initial weight loss (ca. 2 wt%) of functionalized MWCNTs takes place between 50 °C and 150 °C as a result of the evaporation of the adsorbed water on the surface [38]. In the temperature range of 150 °C–350 °C a weight loss of 4.2 wt% (f-MWCNTs-1) and 7.5 wt% (f-MWCNTs-2) occurs, which confirms the decarboxylation process of the carboxylic groups [38, 39]. At elevated temperature (350 °C–500 °C) removal of amorphous carbon on the CNT surface and bonding with OH groups takes place [38, 39], resulting in a mass decrease of 3.0 wt% (f-MWCNTs-1) and 5.1 wt% (f-MWCNTs-2), respectively. At >500 °C a weight loss due to the degradation of the remaining disordered carbon occurs [39].

To obtain a deeper insight into the thermal decomposition behaviour of the functionalized MWCNTs, TG-MS experiments were carried out on the sample of f-MWCNTs-2 under argon as inert atmosphere (figure 5).

As visible from figure 6, evaporation of water at the beginning of the decomposition (50 °C–150 °C) can be confirmed by detection of fragments such as H2O2+ (m/z = 17) (OH−), m/z = 18 (H2O+ and m/z = 44 (CO 2) (argon gas flow 20 ml min−1, heating rate 5 °C min−1).

For analysing the length distribution of the MWCNTs, the SEM images taken as described in 2.1 are shown in figure 7. The SEM images confirm that the acid-treated MWCNTs are more debundled than the untreated CNTs, which is visible from the scattered CNTs visible in figures 6(b) and (c).

This is the result of their functionalization on the surface with, e.g. CO2H and OH groups (figure 7). Furthermore, through acid treatment, shortening of the MWCNTs occurred. The average length of f-MWCNTs-1 is amounted to 0.6 ± 0.3 μm, which is somewhat larger than of f-MWCNTs-2 (0.4 ± 0.2 μm), whereas a narrow length distribution is obtained for f-MWCNTs-2 as compared to f-MWCNTs-1 (figure 8). Compared to functionalization of f-MWCNTs-2...
lower energy input by the preparation of f-MWCNTs-1 was applied resulting in less shortening of MWCNTs.

4.2. Printing results

Both CNT-Isopropanol dispersions were successfully inkjet-printed with different amount overprints on top of silver electrodes. The distribution of CNTs was analyzed with an optical microscope (figure 9). It could be seen that the CNT distribution is not homogeneous. The inkjet print head deposits only showed thin track of material in every single path. The contact line of deposited dispersion is pinned onto the substrate. Since evaporation grade of isopropanol at the edges of a track is higher than in the middle of the track, CNTs are transported to the periphery of the track. This phenomena is known as coffee-ring effect [30]. The self-assembling of MWCNTs after inkjet deposition is also discussed in [40]. The combination of the coffee ring effect and further increasing of the CNTs amount with every new overprint resulted in patterns of a ‘net’ with long ‘threads’ in

Figure 7. SEM images of (a) pristine MWCNTs, (b) f-MWCNTs-1 and (c) f-MWCNTs-2.

Figure 8. Length distribution of (a) f-MWCNTs-1 and (b) f-MWCNTs-2.

Figure 9. Microscopic images of printed sensor on Kapton (left) and magnified CNTs area (right) with different amount CNTs overprints. Print direction from left to right uses f-MWCNTS-1 dispersion.
The print direction. The more material is deposited, the more accumulation can be seen. This picture was common for both dispersions f-MWCNTs-1 and f-MWCNTs-2. Additionally, standalone dots-agglomerates of CNTs, which passed through the nozzles during ejection can be seen.

As expected, the electrical resistance of printed sensors decreases with the amount of deposited material since the amount of conductive material increases (figure 10). Sensor resistance dropped below 1 MΩ already after two overprints for dispersion f-MWCNTs-2 and four overprints for dispersion f-MWCNTs-1. The standard deviation of the resistance between sensors with the same amount of CNTs overprints were not exceed ± 15%. The standard deviation of the resistance depends on the reproducibility and uniformity of the printed layer. As the printed layer is uniform as the standard deviation is very narrow. It is reported that decrease in printing layer will increase the roughness-to-thickness ratio, which in turn decreases in homogeneity of the thin film. As result of decrease in homogeneity, the resistance variations will be more [41]. Additionally, it can be explained that the deposition of very thin film with very low viscous solution will leads to the accumulation of the particles in the edge. This later will conduct to non-uniform and non-reproducible films.

To analyze the topography of printed CNT with profilometry, the CNT-dispersion were printed on a smooth surface of glass (figure 11). High peaks represents the CNTs accumulations. In addition, CNTs are not forming closed layers, due to low loading (concentration of CNTs in isopropanol is only 0.05 wt%) and limited amount of overprints.

4.3. Sensing evaluations

Sensitivity and hysteresis behaviour are among the most important characteristics for assessing humidity sensor performances and selecting the suitable sensing material. The dependence of the resistance on RH is measured for the two sensing materials; f-MWCNTs-1 and f-MWCNTs-2 as shown in figure 12. In this study, 4 layers were printed for each sensing material. According to figure 12, the samples exhibit electronic behaviour where there is a significant increase of resistance in the measurement range when the humidity is increased, which can be attributed to different conduction mechanisms. At low RH, the water molecules are adsorbed by the outer layer of the CNT film. By increasing the RH, the water molecules enter between the CNTs and will be adsorbed on the CNT surface leading to decrease the conduction caused by the enlarged distance between neighbouring CNTs. Then, the absorbed H2O molecules on CNTs sidewall depletes the hole which induces reduced electric conduction in the system. The depletion layer of the CNTs will increase by increasing the RH. It is obvious from figure 12 that the sensitivity of the sensor prepared with f-MWCNTs-2 is higher than the sensitivity of f-MWCNTs-1 which can be correlated to two main effects; the shortness of MWCNTs and the better surface functionalization. Absolutely, short CNTs promote the possibility of water molecules to diffuse into the material as illustrated in figures 13(a) and (b). Where the shortness of MWCNTs is caused from high ultrasonic vibration amplitudes during processing. Given that the CNTs are long, they act more as barriers against the moisture diffusion.
Figure 13. Schematic illustration of the conductive mechanism under humidity and the effect of MWCNTs length (a) long MWCNTs, (b) short MWCNTs and (c) thinner film with thinner CNTs to illustrate the effect of the thickness.

Figure 14. Comparison of humidity responses depending on the number of layers based f-MWCNTs-2.

Figure 15. Repeatability test for sensor based on f-MWCNTs-2 with 10 layers.

Figure 16. Comparison of temperature responses between f-MWCNTs-1 and f-MWCNTs-2.

Figure 17. Comparison of the electrical resistance change depending on the number of layers for f-MWCNTs-1 under temperature changes.
The rate of moisture penetration is becoming large when the humidity sensitivity can be enhanced by adjusting their thickness. To this aim, different samples based on f-MWCNTs-2 were printed with different number of layers (4, 6, 8 and 10 layers) and evaluated at different RH as shown in figure 14. According to figure 14, increasing the number of layers leads to improved sensitivity to humidity and reaches around 669.53 Ω/%RH. The rate of moisture penetration is becoming large when the number of layers is rising caused by the increased water mobility within the CNTs network as shown in figure 13(c). At low RH levels, the main conduction mechanism for the humidity sensor is based on the water adsorption. Therefore, sensor with increased number of layers shows less sensitivity caused by their high surface roughness leading to attach the water molecules in the cavities not on the whole film. Apart from this, the rate of penetration of water molecules will be reduced because of thicker and denser f-MWCNTs-2 films formed in higher printing layers will results less water molecule mobility in CNT films as demonstrated by Kordas et al [43]. However, at high RH, thicker sensors show higher sensitivity to humidity due to the increased pathways for water diffusion. Besides, the presence of more functionalized CNTs will contribute to increase the possibility of water molecules to be absorbed by the CNTs and then to deplete the CNTs as illustrated in figure 13(b). Additional to sensitivity, other parameters such as response, response-recovery time and repeatability are important to ensure the accuracy and efficiency in real applications. Figure 15 illustrates the dynamic humidification and dehumidification cycles of the printed 10 layers sensor measured at RH levels alternated between 11 %RH and 52 %RH at a constant relative temperature of 25 °C. The sample was taken at ambient conditions and placed initially in 52 %RH. From figure 15, it can be seen that the response of the sensor is following the change of humidity. An increase of the resistance during humidification and decrease during dehumidification are observed. Besides, the relative resistance change was around 24%, which demonstrates the repeatability of the printed sensor. From this measurement, the response and recovery time are calculated. It was found that the response time is around 247 s while the recovery is around 96 s which demonstrate the good performance of the humidity sensor.

In order to address the temperature sensing sensitivity, the response of 4 layers printed films prepared with the two different synthesized materials is measured during a single heating/cooling cycle as illustrated in figure 16. This figure shows that the output resistance of both sensors is monotonically increased with increasing the temperature.

The f-MWCNTs-1 sensor shows better performance in terms of sensitivity, stability and low hysteresis comparing to f-MWCNTs-2. Therefore, f-MWCNTs-1 sensor provides reversible response under heating and cooling cycle. The high sensitivity of f-MWCNTs-1 film can be explained due to the increased coefficient of thermal expansion (CTE) by using nano-fillers with longer length. Hwang and Kim [42] demonstrate that the use of material with big grain size results an increase in the CTE. However, f-MWCNTs-1 is sensitive also to humidity. The latter can inhibit the accuracy of the temperature sensor. This behaviour hints about the necessity of compensating the humidity effects by the encapsulation of the sensing material. Before the compensation of the sensor, additional investigation is carried out to determine the appropriate film thickness for higher sensor sensitivity. This study demonstrates as depicted in figure 17 that thinner films are much more sensitive to temperature change owing to the increased possibility for
electron hoping in addition to the increased tunnelling effects caused by the high thermal expansion coefficient of the polymer substrate and the CNTs film layer at low CNTs content.

Without doubt, films based on f-MWCNTs-1 are also sensitive to humidity change. Therefore, it is required to effectively suppress water permeation through the sensing material. In this study, Bectron is used as encapsulation layer. Figure 18 shows that resistance changes depending on the humidity is approximately negligible for the sensor encapsulated with Bectron and it can been seen that encapsulation layer shows the ability to cover all the holes presented within the f-MWCNTs-1 film efficiently leading to inhibit the accessibility of moisture within the film. After proving the efficiency of Bectron layer, the temperature dependency of the encapsulated film is addressed and compared to non-encapsulated film as shown in figure 19.

According to figure 19, the sensor behaviour is changed by the encapsulation layer. The sensitivity to humidity changes is reduced comparing to the non-encapsulated sensor confirming that encapsulation is an efficient way to minimize the effect of humidity in the temperature sensing of the sensors developed in this work. The encapsulated sensor shows higher stability and less hysteresis in both heating and cooling cycles compared to the sensors without encapsulation.

Table 1 shows the comparison of the proposed sensors with previous works. It is clearly seen that the proposed sensors have high relative resistance change in the range of 28% and 80% for temperature and humidity respectively, compared to the sensors adopted in the previous works with very less concentration of CNT (0.05 wt%). This demonstrated the efficiency of the adopted fabrication process for developing highly sensitive and stable humidity and temperature sensors.

### Table 1. Comparison of proposed sensor with previous works.

| Author          | Material                  | CNT concentration wt% | Sensing          | Relative resistance (ΔR/R) |
|-----------------|---------------------------|-----------------------|------------------|---------------------------|
| Catagey et al [44] | CNT                       | 0.5                   | Temperature      | 25%                       |
| Karimov et al [17] | MWCNT                     |                       | Temperature      | 14%                       |
| Honda et al [45]  | CNT/PEDOT:PSS              | 1.3                   | Temperature      | 18%                       |
| Wu et al [3]     | Flake graphite (FG)/carbon nanotube (CNT)/PDMS | 16 | Temperature | 8% |
| **This work**    | f-MWCNTs-1                | 0.05                  | Temperature      | 28%                       |
| Kund et al [46]  | CNT/PANI                  |                       | Humidity         | 40%                       |
| Zhang et al [47] | MWCNT                     | 2.5                   | Humidity         | 55%                       |
| Hajian et al [48] | Fluorinated graphene       |                       | Humidity         | 15%                       |
| **This work**    | f-MWCNTs-2                | 0.05                  | Humidity         | 80%                       |

Functionalization of bundled MWCNTs under acidic conditions (acid mixtures of concentrated H$_2$SO$_4$/HNO$_3$ (ratio 3:1, v/v)) by applying ultrasonication resulted in their debundling and shortening. According to TG measurements, the ultrasonication procedure at higher amplitude (40%) offers a better modification of the MWCNTs surface with CO$_2$H and OH groups. Additionally, the length distribution of f-MWCNTs-2 is narrower as for f-MWCNTs-1.

Inkjet technology was proven to be suitable for the fabrication of sensors based on CNT-isopropanol dispersions. CNTs on top of silver electrodes had a tendency to form a ‘net’ and to self-assemble in ‘threads’ in parallel to print direction. Nevertheless, the initial resistance of printed sensors was not deviated more than ±15% for the sensors with the same amount of CNTs overprints.

Novel resistive humidity and temperature sensors based on the use of MWCNT-COOH coated on interdigital microelectrodes are proposed. The performance of the sensor has been influenced by the degree of functionalization and the process used for functionalization.

The increase of dispersing energy (sonication amplitude) leads to enhance the humidity sensitivity due to the CNTs shortening that results in larger accessibility of the water molecules diffusing into the sensor. In addition, it was shown that the overall sensitivity can be tailored by increasing the number of printed layers. The developed sensor exhibits good humidity sensitivity $669.53 \, \Omega/\%$RH at different RH levels from 11 %RH to 97 %RH in addition to high sensor linearity over this range. Meanwhile, good sensor performance is also achieved during dynamic humidification and de-humidification demonstrating the efficiency of the printed process. As well, the printed humidity sensor has demonstrated a good response time $\approx 247$ s and recovery time $\approx 96$ s. An inverse effect for temperature sensing is observed with the use of high sonication amplitude. In fact, low sonication amplitude maintains the length of CNTs long, which promotes larger thermal expansion coefficient. In addition, a successful compensation of humidity effect was performed by using Bectron layer. The approach followed in this work provides an efficient route to achieve highly sensitive resistive and cost-effective humidity and temperature sensors with less material amount and waste and high reproducibility.
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