

# Facile Fabrication of Hybrid Carbon Nanotube Sensors by Laser Direct Transfer

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## Research Article

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## Facile fabrication of hybrid carbon nanotube sensors by laser direct transfer

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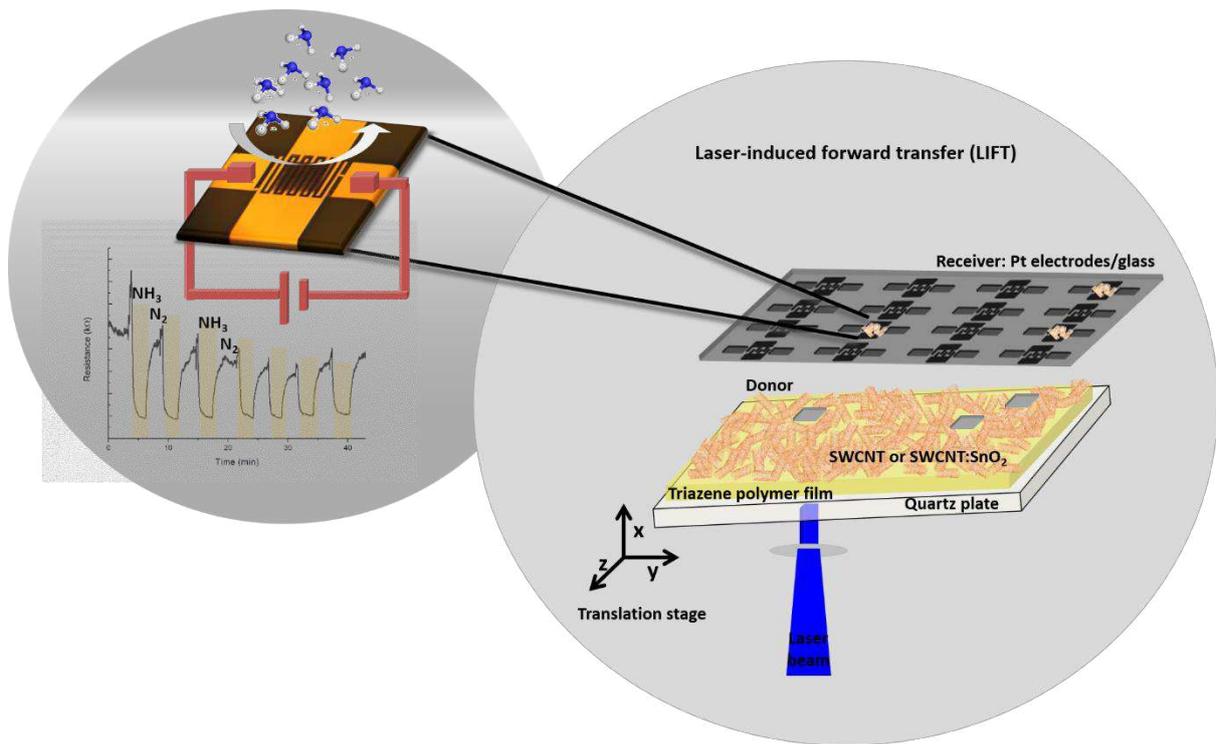
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### Abstract

This paper describes a rapid, solvent-free laser based procedure for the fabrication of reproducible sensitive sensors based on hybrid nanocomposites, i.e. single walled carbon nanotubes (SWCNTs) decorated with tin oxide nanoparticles (SnO<sub>2</sub> NP) that overcomes challenges associated with solvent-assisted chemical functionalization and integration of these materials into devices.

The gas response of the LIFT-ed SWCNT: SnO<sub>2</sub> sensors has been evaluated at room temperature and an enhanced 2 fold response to ammonia as compared to the SWCNT sensors is demonstrated. Spontaneous and full recovery of the hybrid nanocomposite signal after exposure to NH<sub>3</sub> is achieved without any post treatment. The theoretical detection limit of the LIFT-ed SWCNT: SnO<sub>2</sub> sensors at room temperature is calculated to be 0.59 ppb. These results indicate that LIFT is an excellent technique which shows great promise towards advancing future developments in the field of chemical sensors.

## Graphical Abstract



## Introduction

The detection of chemicals such as ammonia, methane, nitrogen oxides, bleach, salts, nitrites, pesticides, metals, etc. is a subject of research for more than 20 years. In particular, ammonia ( $\text{NH}_3$ ) is one of the most frequently produced industrial chemicals in the United States and China [1]. It is extensively used in various industrial applications, i.e. production of fertilizers, plastics, dyes, etc. Exposure to high concentrations of ammonia in air causes bronchiolar and alveolar edema, whilst the inhalation of lower concentrations can cause coughing, nose and throat irritation [2]. Ammonia's odor provides adequate early warning of its presence; however, ammonia also causes olfactory fatigue or adaptation, reducing awareness of one's prolonged exposure at low concentrations [3]. According to the National Institute for Occupational Safety and Health (NIOSH) the acceptable exposure limit is of 25 ppm for 8 hours period and 35 ppm for 15 minutes exposure.

Therefore, detection of ammonia requires efficient devices with several key characteristics, i.e. sensitivity, the minimum concentration of target gases they can detect, response speed, reversibility, energy consumption, and fabrication costs [4].

For the last 50 years, the field of sensors has been dominated by the metal oxide semiconductor sensors (MOS) based on  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{ZnO}_2$ ,  $\text{WO}_3$ , etc. [5]. This type of sensors have numerous advantages in terms of raw material costs, high sensitivity, etc.. However, their main disadvantage is that they have to be operated at higher temperatures (e.g.  $\text{SnO}_2$  at 500 °C) which makes difficult their application on flexible substrates (usually polymers) [6]. For example, in our previous work we could show that it is possible to detect small amounts of ammonia (50 ppm) using sensors based on  $\text{WO}_3$  thin layers fabricated by pulsed laser deposition. The sensors (operated at 300 °C [7]) work well, their response towards ammonia is larger than of the sensors fabricated by more conventional methods such as thermal evaporation or chemical routes. In addition, the  $\text{WO}_3$  based sensors have a reproducible response over multiple  $\text{NH}_3/\text{N}_2$  exposure cycles.

The field of sensors is far from mature, and since the pioneering work of Dai and coworkers [8] where the first examples of single walled carbon nanotube (SWCNT) chemical sensors were reported, sensors based on CNT have gained great interest. Resistive SWCNT based sensors are low power devices, ideal for direct electrical detection, i.e. their conductance changes upon adsorption of an analyte, i.e. gas molecules [9]. In gas sensing applications, SWCNTs have been demonstrated for the detection of common organic vapors, [10] oxidizing vapors such as  $\text{Cl}_2$  or  $\text{NO}_2$ , [11] and even trinitrotoluene (TNT) [12] and chemical warfare agents [13]. The main drawbacks for the application of SWCNT in sensors are the high price and the necessity to find techniques to deposit them on the active area of a resistive sensor with high enough conductivity [14].

Although there are numerous examples of sensors based on pristine CNTs, different reports available in literature [15] associate an increased sensor response and sensitivity towards different analytes to residual metal catalysts or particles from the production process. Thus, hybrid carbon-based sensing

materials can be developed by intentionally decorating or doping carbon nanotubes with metal nanoparticles in order to produce a stronger and specific response towards the analytes of interest [16]. In fact, in this work we focus onto an easy and straight forward sensor device fabrication strategy that relies on laser printing of the sensing materials i.e. hybrid carbon nanotubes (SWCNT decorated with SnO<sub>2</sub> nanoparticles).

The laser-based method applied here is laser-induced forward transfer (LIFT). LIFT is a clean (solvent free) and versatile fabrication method, which has already been applied for device fabrication [17, 18]. The basic principle of LIFT relies on shaping and projecting a laser beam onto a donor substrate coated with the material to be transferred. The donor substrate coated with the material to be transferred is then placed parallel and at a controllable distance to a receiving substrate and the entire system is moved with respect to the fixed laser beam so that it is possible to “write” arbitrary patterns. Laser transfer of material takes place when a single laser pulse is fired. The main advantage of LIFT is that large area donor substrates can be prepared by standard thin film techniques such as spin-coating, evaporation, or sputtering. From the large donor substrate, a selective transfer of only a small part defined by the laser spot can be achieved, without any additional photolithography step. Using this configuration, the laser interacts with the material to be transferred and only insensitive materials like metals or ceramics can be transferred. In order to transfer more sensitive materials, i.e. which can be damaged by the laser beam (generally “soft” materials such as proteins or polymers), the LIFT process needs to be improved by adding an intermediate layer between the donor substrate and the material to be transferred. This layer, named sacrificial layer or dynamic release layer has the role to protect the material to be transferred from the applied laser light and generated heat.

Furthermore, LIFT has also the potential to allow for a material usage in the range of 80% and even more importantly, it is possible to utilize layer-like structures such as the hybrid SWCNT:SnO<sub>2</sub> nanocomposite, a task difficult to achieve with other deposition methods.

Few examples of carbon nanotube transfers have been reported previously, i.e. in [18] we have proved that it is possible to transfer SWCNT by LIFT with the goal of fabricating chemoresistive sensors. Once the process parameters have been optimized, the functionality of the as-fabricated sensors has been demonstrated by detection of different ammonia concentrations in the ppm range. Furthermore, in [19] the authors demonstrated the possibility to print polymer-multiwalled carbon nanotube composites by LIFT, whilst in [20] the authors demonstrated the transfer of SWCNTs and SWCNTs embedded in a polymer matrix by a modified LIFT process, i.e. using a blister to mechanically deform the donor layer. Moreover, in [21] the authors presented the possibility to LIFT and decorate multiwalled carbon nanotubes with gold–palladium nanoparticles, and demonstrated the adsorption characteristics towards hydrogen. However, their approach has some disadvantages, i.e. the decoration is not homogeneous, and for a higher number of laser pulses, the CNTs suffer a structural and chemical degradation.

Therefore, in this study, we focus on transferring hybrid SWCNT i.e. decorated with tin oxide nanoparticles (SWCNT:SnO<sub>2</sub>) with the purpose of obtaining improved and reproducible resistive

sensors. Although there are several reports on reversible  $\text{NH}_3$  sensing using chemiresistors based on SWCNT:SnO<sub>2</sub>, the fabrication methods for such sensors are not cost effective. In addition, thermal treatments or photo-irradiation is often required to desorb the vapor again for reversible operation of the sensor [9]. Thus, here we report for the first time the fabrication of resistive sensors by laser-induced forward transfer of hybrid nanocomposites, i.e. SWCNT:SnO<sub>2</sub> with a detection limit towards ammonia below 1 ppb.

## Results and Discussion

### LIFT printing

The gas sensing mechanism of the sensors is dependent upon multiple factors including the surface of the active material; therefore, the analysis of the donor films morphology is conducted first. Following our donor fabrication strategy shown in Fig.1 we could spin coat randomly oriented SWCNTs arranged in curly bundles (see Fig. 2 a). In addition, several  $\mu\text{m}$  long carbon nanotube bundles with diameter ranging from 30 to 70 nm and SnO<sub>2</sub> NP which agglomerate in clusters with dimensions of 10 to 15 nm anchored to the SWCNT surface in the hybrid donor materials can be seen in the SEM images shown in Fig. 2 b). The SnO<sub>2</sub> NPs are regularly distributed on the SWCNT as shown in Fig. 2 b). However, in some areas, the SnO<sub>2</sub> NPs are specifically agglomerated at points where the carbon nanotubes have a close bond, which has also been seen in our previous work [22], where the NPs were agglomerated at defect points onto the surface of carbon nanowalls.

The transfer of pixels in a controlled manner, and an insight on the morphological properties of the LIFT-ed single walled carbon nanotubes and hybrid SWCNT:SnO<sub>2</sub> are essential in applications aimed at practical devices. Once pixel deposition is possible, controlled printing and regular pixel deposition can be achieved. In our previous work [18] we have investigated different LIFT process parameters, i.e. the TP thickness as well as the laser fluence applied for the transfer in order to obtain regular SWCNT patterns. Furthermore, in order to prove that LIFT is a suitable technique to be used for device fabrication, SWCNT have been transferred onto Pt electrodes, and concentrations as low as 50 ppm of ammonia have been detected. However, more work is needed to optimize the process and also to obtain better sensor response, i.e. for consistent monitoring of acceptable concentrations of  $\text{NH}_3$ .

Here we show that it is possible to transfer regular SWCNT:SnO<sub>2</sub> with the help of a 150 nm thick TP DRL layer (see Fig. 3). Transferring SWCNT:SnO<sub>2</sub> by LIFT is possible leading to sharp pixels, the best transfers is achieved with a laser fluence of 300  $\text{mJ}/\text{cm}^2$  (similar to the transfer of bare SWCNTs at 250  $\text{mJ}/\text{cm}^2$  in [18]). The overall appearance of the pixel is rather “microporous” than homogeneous, however, indicating a complete layer of SWCNT:SnO<sub>2</sub>. Additionally, the transfer fluence of 700  $\text{mJ}/\text{cm}^2$  is comparably high and for lower fluence no complete layer transfer was achieved. As it can be seen reproducible transfers with an intermediate 150 nm thick TP layer and a laser fluence of 300  $\text{mJ}/\text{cm}^2$  is achievable.

In addition, pixels are transferred at  $300 \text{ mJ/cm}^2$  laser fluence onto sensor like pads and the electrical characteristics and sensing abilities toward ammonia are tested further. The electrode design and an image of a LIFT printed sensor-like pad is shown in Fig. 4.

The transfers onto the IDT structure do not show significant differences from the transfers onto the glass part. An example of a SWCNT:SnO<sub>2</sub> pixel transferred onto a sensor like pad is shown in Fig. 4. After the transfer, the as fabricated sensors are conditioned as described above in order to cure the transferred material. During LIFT, the high velocities generated (around 200 m/s) [17] lead to firm electrical contact between the electrodes and pixels, allowing better draining of the injected carriers through the electrodes.

These data show that LIFT transfers onto different substrate materials work very well. Transferring onto the IDTs with a structure height comparable to the film thickness shows a similar behavior as the transfers on the even surfaces. Even transfers of SWCNT:SnO<sub>2</sub> pixels with a film thickness smaller than the IDTs structure height proved to be possible.

### **Sensor tests**

The scope of this study is to demonstrate the fabrication of proof-of-concept sensors by directly printing hybrid nanocomposite materials via laser-based techniques as active materials in sensor devices. Here we focus on investigating the functionality of the laser transferred active materials onto sensor structures by evaluating their potential to detect small amounts of ammonia at temperatures close to room-temperature in synthetic air.

The first step is to evaluate whether there are any variations in the baseline of the laser printed sensors when exposed to a constant synthetic air flow. For the SWCNT printed sensors the baseline resistance drift at room temperature in synthetic air is insignificant (see Fig. 5 a). For the SWCNT:SnO<sub>2</sub> printed sensors the baseline resistance drift at room temperature in synthetic air has a small drift, however below 2% (see Fig. 5 a). This can be explained by the nature of electrical contact between metal electrode (i.e. Pt) and sensing element [23]. The baseline resistance (two-points electrical measurement) is typically between 2 and 15 kOhms, a resistance range very applicable for sensors and much lower than the Megaohm range found for sensors with standard SWCNT [11].

For comparison, the gas-sensing properties of the sensors based on LIFT-ed SWCNT and SWCNT:SnO<sub>2</sub> pixels to 50 ppm ammonia concentration are shown in Fig. 5 b). During the measurements, the temperature T is continuously measured for the SWCNT and SWCNT:SnO<sub>2</sub> ( $T=25 \pm 2 \text{ }^\circ\text{C}$ ).

The first observation which can be made is that after exposure to NH<sub>3</sub>, the resistance of the SWCNT:SnO<sub>2</sub> sensor immediately decreases, and gradually approached a steady state over a period of ~ 2 minutes, thus showing a n-type response to NH<sub>3</sub>. In contrast, the SWCNT sensors show a p-type response to NH<sub>3</sub>, i.e. after exposure to NH<sub>3</sub>, the resistance of the sensors increases from approx. 6.5 kΩ to 9 kΩ. This effect has been seen previously [9,11] to SWCNTs which are exposed to reducing

molecules. Briefly, when the surface of the SWCNTs is exposed to the reducing  $\text{NH}_3$  molecules, the accumulation region is reduced, yielding a decrease of the hole current, i.e. an increase of the resistance, shown by the SWCNT sensors printed by LIFT.

In addition, the SWCNT: $\text{SnO}_2$  sensor response is reproducible over multiple analyte/ synthetic air exposure cycles (see Fig. 5 b). Very important, the signal recovered to the original baseline value upon removal of the  $\text{NH}_3$ .

In order to evaluate the performance of our printed sensors, we investigate several key factors: i) the sensor response to ammonia, which is defined as  $\Delta R/R_0=(R_g-R_0)/R_0$ , where  $R_g$  is the resistance upon  $\text{NH}_3$  exposure and  $R_0$  the baseline resistance before exposure to  $\text{NH}_3$ ; ii) the response and recovery times which are defined as the times for the sensor to reach 90% of its maximum and to recover 10% of its peak value upon exposure to a given concentration of  $\text{NH}_3$ . In order to reproduce realistic conditions, after being exposed to each  $\text{NH}_3$  concentration, the testing chamber has been unsealed and the sensors have been allowed to recover at room temperature in laboratory conditions.

The SWCNT sensor response is characterized by a steep increase in short time and when the analyte is removed by a slower decrease. Although both SWCNT and SWCNT: $\text{SnO}_2$  sensors display a resistivity change, both the response and recovery appear to be much slower in the case of SWCNT with respect to the hybrid nanocomposite SWCNT: $\text{SnO}_2$  sensors. The better sensor response of the SWCNT: $\text{SnO}_2$  sensors as compared to the SWCNT sensors to  $\text{NH}_3$  analyte (see Fig. 5 c), could be attributed to a sum of factors, i.e. the enhancement of the surface area accessible to the ammonia molecules, and possibly to the formation of p-n junctions between the semiconducting metal oxide NP and the CNT bundles. In literature, there are many studies focused on the gas sensing mechanism in n-type semiconducting metal oxide nanoparticles and p-type carbon nanotubes, where these materials are combined to form p-n junctions. The case of p-n junctions between p-type SWCNTs and n-type semiconductor NP has been presented on hybrid SWCNT:NP [24], however, a clear understanding of the mechanisms leading to gas sensing has not yet been reached [25].

A brief evaluation of the recovery and response times for the different types of sensors evaluated in this work and a comparison with other types of sensors based on carbon and tin oxide, which are exposed to different concentrations of ammonia is shown in Table 1. The results we present in this work show that showed that the printed hybrid SWCNT: $\text{SnO}_2$  are promising candidates for the fast detection of  $\text{NH}_3$  at room temperature.

Furthermore, due to the limitations of our experimental setup, concentrations as low as 5 ppm could be detected in synthetic air without any external aid such as thermal or photoirradiation (see Fig. 5 d). Therefore, we have calculated the theoretical detection limit (LOD) as previously reported [11, 30] from the signal / noise ratio. First, we took 13 data points at the baseline before  $\text{NH}_3$  exposure ( $y_i$ ) and plotted the data using a fifth order polynomial fit. From the curve-fitting equation we obtained the statistical parameters of the polynomial fit ( $y$ ), and then calculated the sensor noise using the root-mean-square deviation (Eq. 1).

$$\text{Eq. (1) } \text{rms}_{\text{noise}} = \sqrt{\sum (y_i - y)^2 / N}$$

where N is the number of data points in the curve fitting. The  $\text{rms}_{\text{noise}}$  for the SWCNT:SnO<sub>2</sub> sensor is 7.09599E-5. The theoretical detection limit according to IUPAC is  $\text{LOD} = 3 \times \text{rms}_{\text{noise}} / \text{slope}$ . The slope is obtained from the calibration curve of the sensor response in Fig. 5 e). For the LIFT printed SWCNT:SnO<sub>2</sub> sensors we obtained a LOD = 0.59 ppb, which is well below the eight-hour permissible exposure limits to NH<sub>3</sub> of 25 ppm as stated by the Occupational Health and Safety Administration's (OSHA).

Therefore, the approach presented here, of combining special materials in the form on carbon nanotube based nanocomposites and the designed polymer absorbers for the laser-based printing, combined with an advanced laser direct write approach is very attractive to advance the state-of-the-art in sensing devices.

## **Experimental**

### **Preparation of the materials to be transferred – donor fabrication**

The materials to be transferred by laser-induced forward transfer are single-walled carbon nanotubes (SWCNT, HiPco) purchased from Nanointegris and hybrid nanocomposites based on SWCNT and SnO<sub>2</sub> nanoparticles from Alfa Aesar.

The SWCNT are used as received, without any additional purification step. Dispersions of SWCNT in water are realized by suspending 10 mg CNT powder in 15 ml water containing 100 mg Triton X. The SnO<sub>2</sub> nanoparticles used in this work have a nominal particle size of 10 - 15 nm and are dispersed in a colloidal solution at a concentration of 14 w% in water. The dispersion is bath sonicated for 40 min.

The hybrid SWCNT:SnO<sub>2</sub> nanocomposites are prepared by dispersing the HiPco SWCNT in the SnO<sub>2</sub> NP solutions by ultrasonic vibration for about 2 h to obtain the well-mixed suspensions.

The preparation of the TP layer, the SWCNT and hybrid SWCNT:SnO<sub>2</sub> layers is carried out following the procedure described schematically in Fig. 1.

In order to prepare the donor films for the LIFT experiments a preliminary step of coating fused silica plates with a photosensitive polymer, i.e. a triazene polymer (TP), is carried out. The specific triazene polymer is synthesized following the procedure published previously [31]. The triazene polymer is deposited by spin-coating from a 2% wt solution of chlorobenzene and cyclohexanone (1:1 w/w). The TP containing solution is dispensed onto the substrate through a 0.45 μm filter. Spinning is carried out for 60 s at a speed of 2000 rpm with a ramp of 1000 rpm/s. The films are dried after deposition for 2 hours at 50 °C. Films with a thickness of 150 nm are obtained with this procedure.

The SWCNT and SWCNT:SnO<sub>2</sub> layers are fabricated by spin coating the SWCNT and SWCNT:SnO<sub>2</sub> dispersions (different experiments) onto TP-coated fused silica plates under different conditions, i.e., rotation speed 1500–2500, ramp of 1000–2000 rpm, and spin-coating duration of 30 and 60 s. Once the

final donor layers are obtained, a post heating step (60 °C for 4 hours) is applied to remove the residual solvent from the film.

## **LIFT**

The LIFT setup used in this work has been detailed in our previous works [6, 18] and it consists of a pulsed XeCl laser (308 nm emission wavelength, 30 ns pulse length, 1 Hz repetition rate) which is guided and imaged with an optical system at the quartz substrate - TP layer interface and as a result of the rapid increase in pressure at the quartz-TP interface a part of the donor layer (SWCNT or SWCNT:SnO<sub>2</sub>) is transferred (further named pixel) onto the receiving substrate. A computer-controlled *xyz* translation stage allows the displacement of both donor and receiving substrates with respect to the laser beam. The donor and the receiving substrates are kept in contact. All experiments are carried out under ambient pressure at temperatures close to room temperature.

As receiver substrates we are using both glass coverslips cut into 25 × 25 × 1 mm<sup>3</sup> pieces for the post-characterization of the transferred pixels as well as interdigitated (IDT) electrodes. The IDT electrodes have a similar structure to the commercial sensors (Microsens gas sensor, MSGS 3000). Briefly, the IDT electrodes are fabricated by sputtering a 20 nm chromium layer followed by a 100 nm platinum layer on top onto a borax glass substrate [6].

In order to obtain a stable sensor response, the LIFT printed sensors are subjected to a heating treatment, similar to the commercial sensors. The LIFT-ed sensors are heated for 6 h at 150 °C followed by 6 h at 100 °C in a stream of 1 l/min of synthetic air (SA) containing 20% O<sub>2</sub> and 80% N<sub>2</sub>.

The transferred SWCNT and SWCNT:SnO<sub>2</sub> pixels as well as the donor films prior to ablation are investigated by optical microscopy. The images are acquired with an Olympus SZH 10 Research Stereo microscope coupled with a Stingray F145C CCD camera.

The distribution of the SWCNT and SWCNT:SnO<sub>2</sub> prior and after their deposition by LIFT is investigated by scanning electron microscopy (SEM). The images are obtained from top view SEM and are acquired with a Zeiss Supra VP55 FE-SEM apparatus operating at a voltage of 5kV and using an in-lens detector.

## **Sensor testing setup**

The functionality of the LIFT-ed SWCNT and hybrid SWCNT:SnO<sub>2</sub> based sensors is assessed in a setup which has been described previously in [6]. Briefly, the sensor testing setup consists of a sensor testing chamber provided with a constant gas supply, where the sensors are mounted on an alumina block and are contacted electrically by two metal clamps, on the side pressing a graphite rod onto the Pt-electrodes reaching a total contact resistance of less than 50Ω. Graphite rods are needed to prevent the Pt-electrodes to be scratched off [6]. The resistance measurements are acquired by a computer controlled (LabView) setup using a Keithley 2400 source meter and Keithley 2000 multi meter. The

main gas supply is synthetic air (SA) consisting of dry 80% N<sub>2</sub> and 20% O<sub>2</sub>, with a standard gas flow of 5 l/min SA.

In order to test the LIFT-ed SWCNT and hybrid SWCNT:SnO<sub>2</sub> based sensors for their ability to detect NH<sub>3</sub>, defined concentration of NH<sub>3</sub> are mixed in a balloon from Carl Roth and added in small quantities to the main gas stream. This mixture is added with a low flow rate (0.01 to 0.1 l/min) to the main gas flow and analyte concentration in the ppm range are thus achieved [6].

## **Conclusions**

In summary, we have successfully demonstrated the „clean“ solvent free fabrication of SWCNT:SnO<sub>2</sub> nanocomposite based sensors. Hybrid nanocomposites, i.e. SWCNT:SnO<sub>2</sub> were transferred with high resolution onto specific metallic geometries designed onto glass substrates. The resulting sensors exhibit high responses to ammonia at room temperature, and the theoretical detection limit is in the low ppb range (i.e. 0.59 ppb). Moreover, the LIFT-ed SWCNT:SnO<sub>2</sub> nanocomposite sensors have a negligible baseline drift, are reusable, and the sensor response is reversible over multiple cycles.

The advantages of the LIFT-ed sensors based on SWCNT:SnO<sub>2</sub> nanocomposites as compared to the SWCNT sensors could be due to an efficient electron transfer between the SnO<sub>2</sub> nanoparticles and the SWCNTs and, in addition, to the increase of the specific surface area of the hybrid nanocomposites.

In perspective, this study provides an opportunity to fabricate sensors by a simple technique, compatible with a scale-up process, for monitoring of sub-ppm ammonia concentrations. The fast response and recovery times together with the low detection limit required for realistic monitoring of ammonia concentrations are achieved. Thus, the implementation of SWCNT:SnO<sub>2</sub> laser printed sensors that can provide a reliable monitoring of NH<sub>3</sub> represent the basis for future advanced sensing devices.

Future studies focused on understanding i) the interaction of the laser beam with hybrid nanocomposites and ii) the underlying mechanism of hybrid nanocomposite sensing of reducing and oxidizing gases are envisioned for developing new and innovative electronic devices and sensing arrays.

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## **Competing interests**

The authors declare no competing interests.

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### Figure caption

**Fig. 1** Scheme of the LIFT setup: step 1 – 5 fabrication of the donor substrate by spin coating and step 6 transfer by LIFT of the donor material (SWCNT:SnO<sub>2</sub>) onto the receiver substrate (glass plate with Pt electrodes). Step 1: The donor plate is placed in the spin coater. Step 2 and 3: The quartz plate is coated with a thin film of the triazene polymer (TP). Step 4 and 5: The SWCNT:SnO<sub>2</sub> suspension is spin coated onto the TP/quartz plate. Step 6: The donor and receiver are placed onto a xyz translation stage. The laser beam impinges through the transparent quartz plate, vaporizes the TP which mechanically pushes forward a small portion of the SWCNT:SnO<sub>2</sub> film onto the glass plate with Pt electrodes.

**Fig. 2** Representative SEM images of a) SWCNT and b) SWCNT:SnO<sub>2</sub> donors as fabricated, prior to laser transfer.

**Fig. 3** SWCNT:SnO<sub>2</sub> microarray transferred by LIFT by keeping in contact the donor and receiver substrates.

**Fig. 4** Optical microscopy images of a) the interdigital electrodes and b) a SWCNT:SnO<sub>2</sub> pixel printed onto the metal electrodes. c) SEM image of SWCNT:SnO<sub>2</sub> pixel transferred by LIFT at 300 mJ/cm<sup>2</sup> laser fluence onto the sensor IDTs, and d) SEM image taken at a higher magnification of a SWCNT:SnO<sub>2</sub> pixel transferred by LIFT at 300 mJ/cm<sup>2</sup> laser fluence onto the sensor IDTs, where the SnO<sub>2</sub> nanoparticles decorating the SWCNTs can be seen.

**Fig. 5** a) Resistance vs time profile for LIFT-ed SWCNT and SWCNT:SnO<sub>2</sub> pixels before exposure to different concentrations of NH<sub>3</sub>. A stable 6 h baseline is depicted. b) Reproducibility of the SWCNT and SWCNT:SnO<sub>2</sub> sensors response printed by LIFT to 50 ppm of NH<sub>3</sub>. c) Comparison of the SWCNT:SnO<sub>2</sub> and SWCNT response to NH<sub>3</sub> at 50 ppm. d) Real-time measurements of a SWCNT:SnO<sub>2</sub> sensor printed by LIFT collected for different concentrations of NH<sub>3</sub>. e) SWCNT:SnO<sub>2</sub> sensor response as a function of NH<sub>3</sub> concentration at room temperature in air depicting a good linear relation.

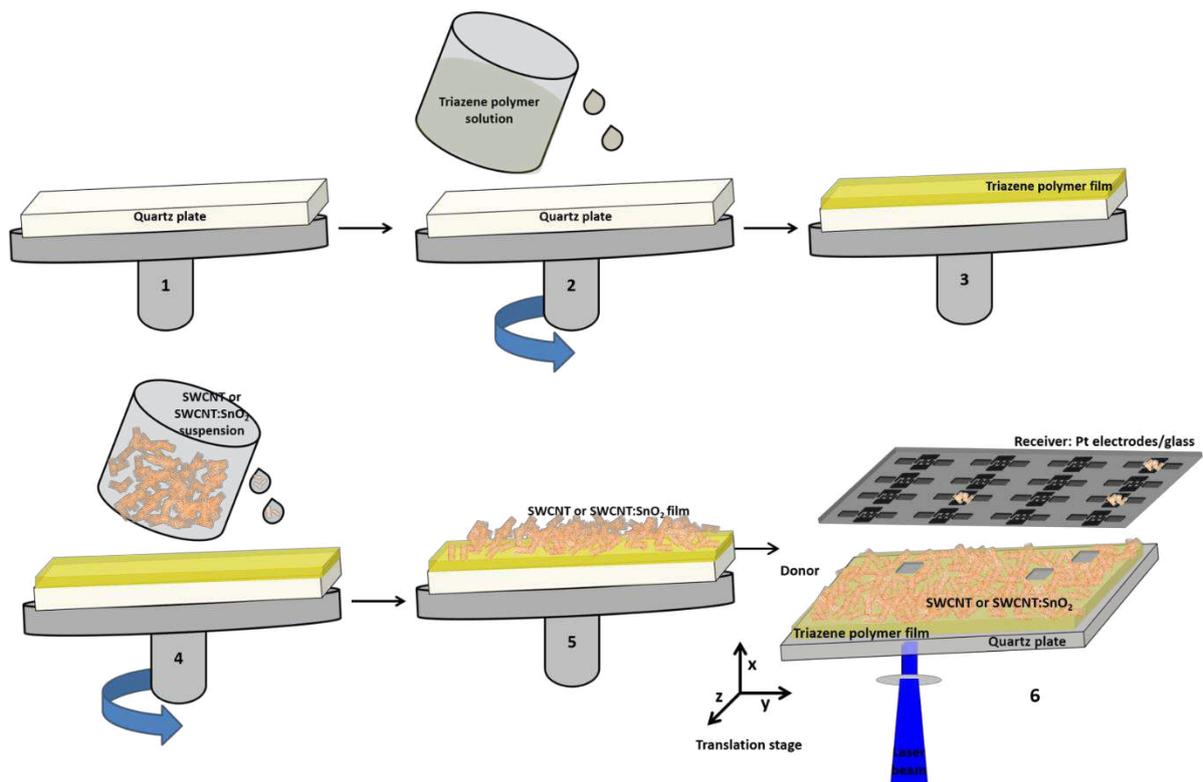
**Table caption**

**Table 1** Summarized sensor parameters for different works as compared to the SWCNT and SWNT:SnO<sub>2</sub> sensors fabricated by LIFT

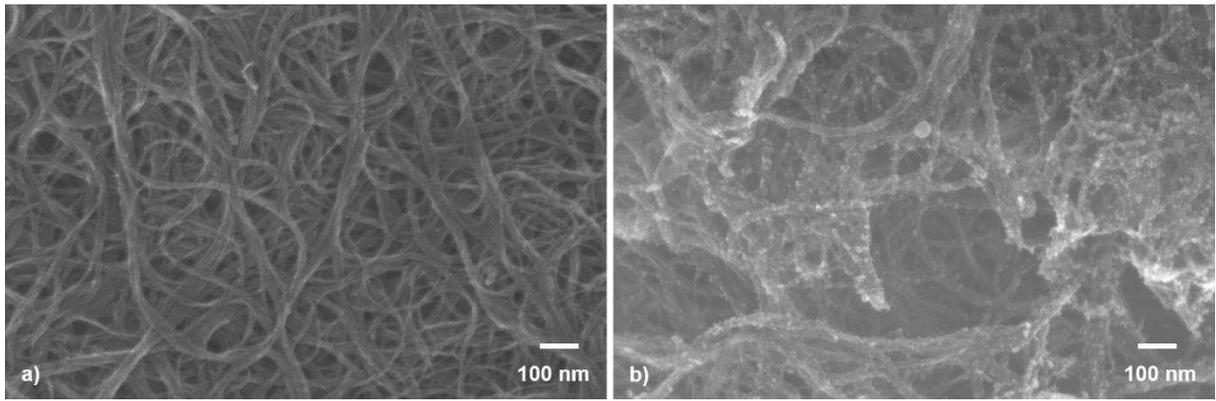
**Table 1**

<b>Sensing material</b>	<b>Operating temp. (°C)</b>	<b>Concentration (ppm)</b>	<b>Sensor response %</b>	<b>Response time</b>	<b>Recovery time</b>	<b>Ref.</b>
SWCNT:SnO <sub>2</sub>	RT	50	0.82	65 sec	44 sec	This work
SWCNT	RT	50	0.43	174 sec	12 min	This work
SnO <sub>2</sub> + 1%wt MWCNT	220	60	0.19	> 100 s	> 100 s	[26]
SnO <sub>2</sub> /SWNT	RT	50	0.53	15 min	20 min	[27]
SnO <sub>2</sub> /SWNT	RT	100	0.1	5 min	> 30 min	[28]
SnO <sub>x</sub> -SWNT	200	1000	0.81	1.62 min	3.14 min	[29]
SnO <sub>2</sub> + 15% MWCNT	RT	200	0.27	< 5 min	< 5 min	[30]

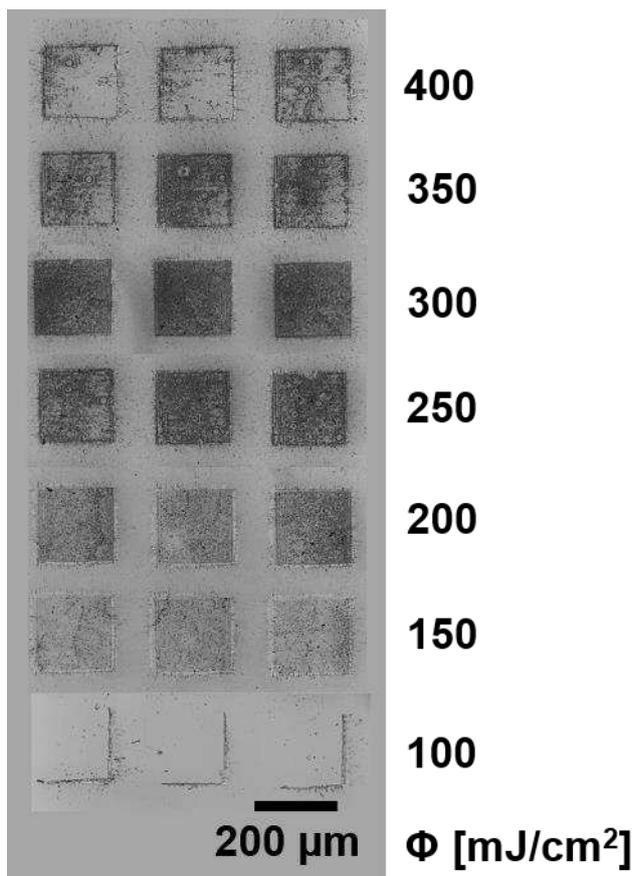
Fig. 1



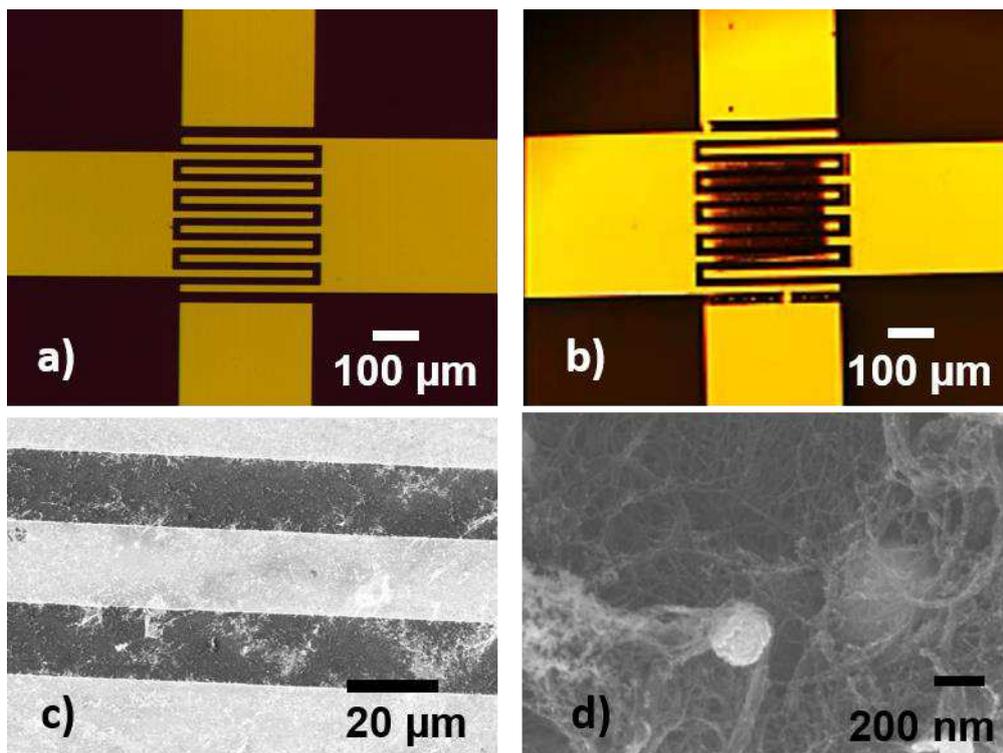
**Fig. 2**



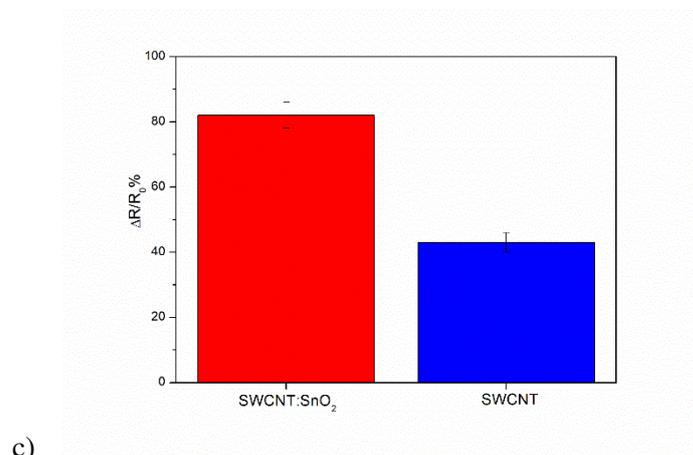
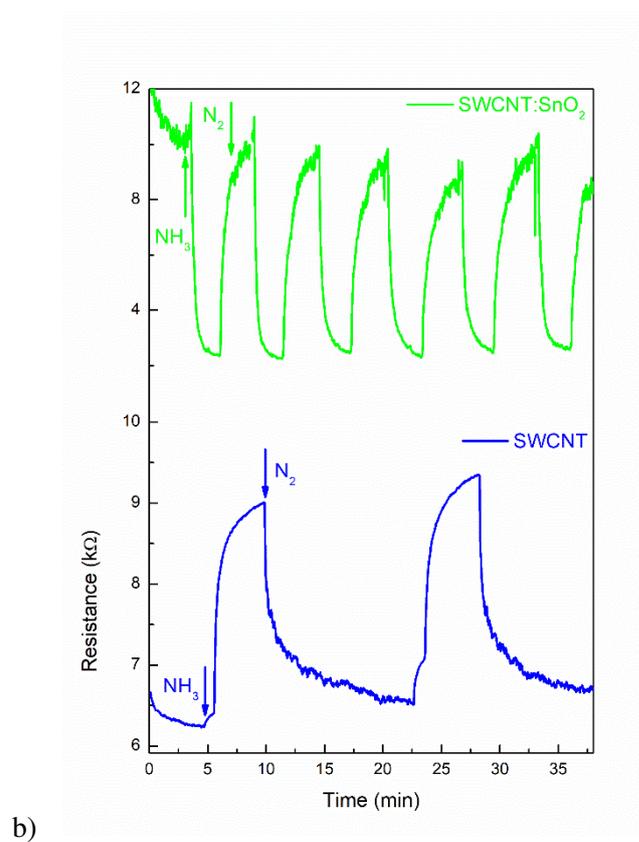
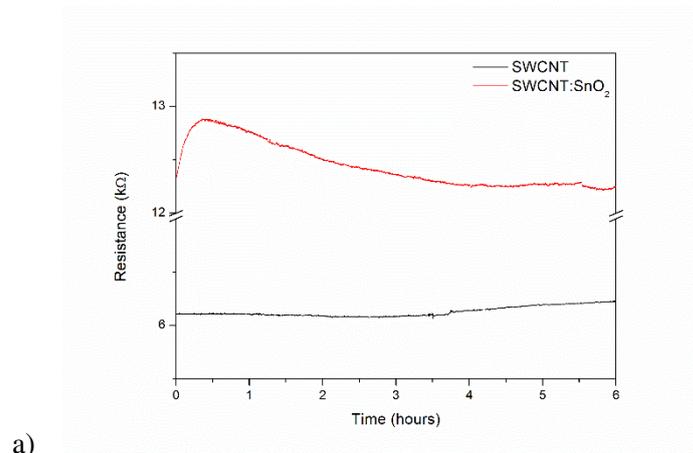
**Fig. 3**

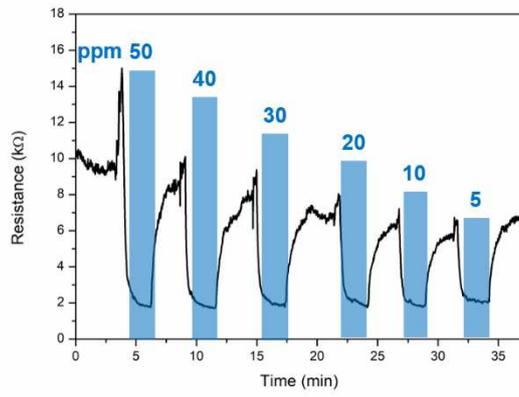


**Fig. 4**

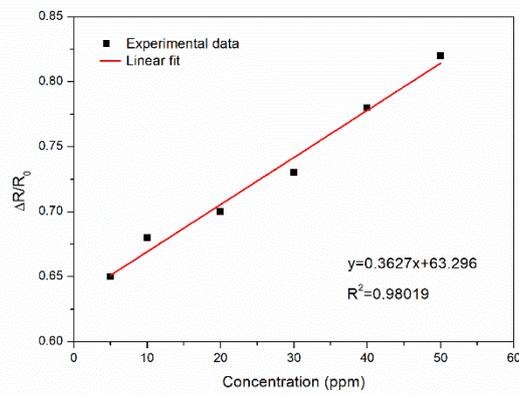


**Figure 5**





d)



e)

# Figures

Fig. 1

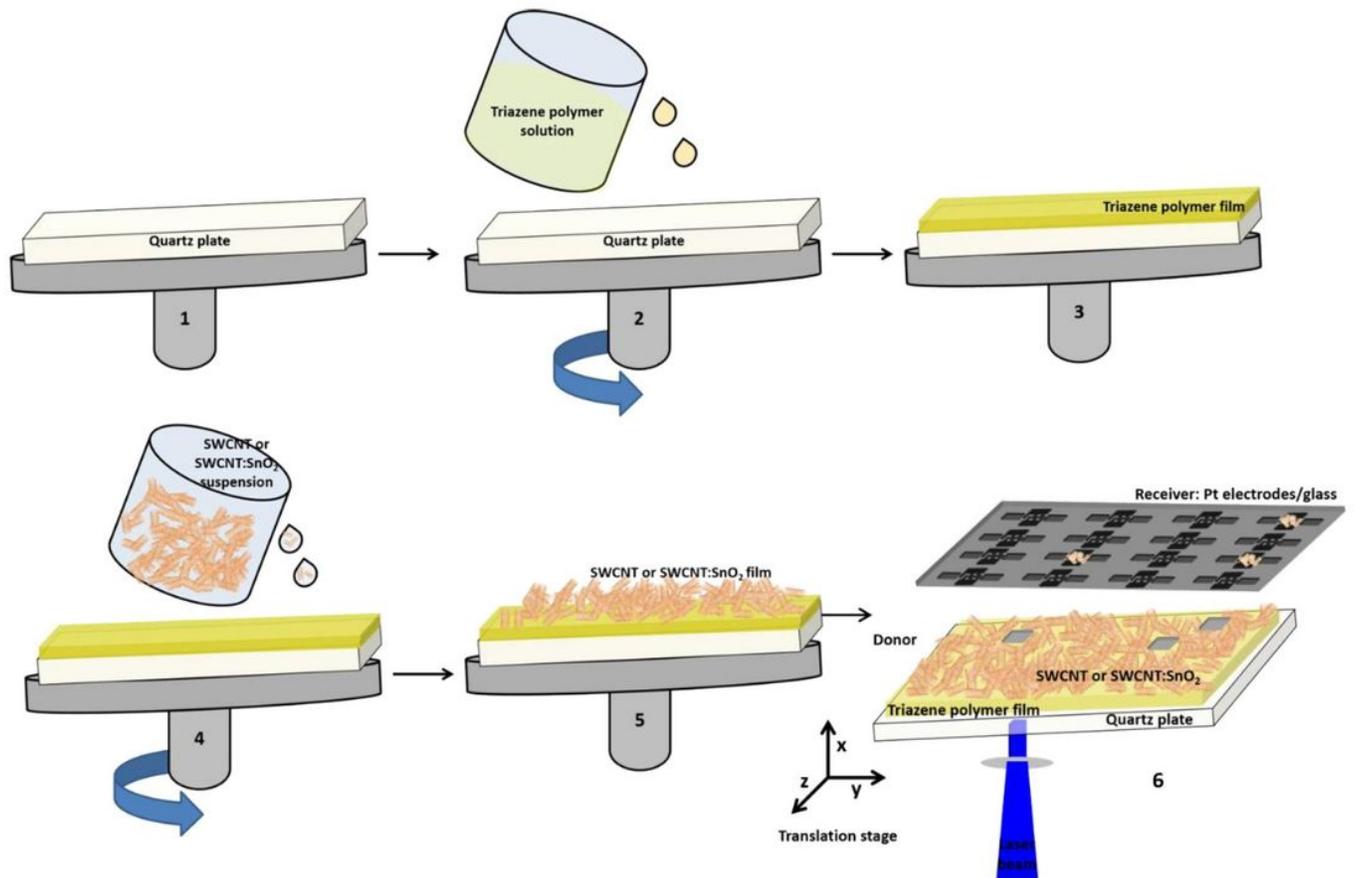
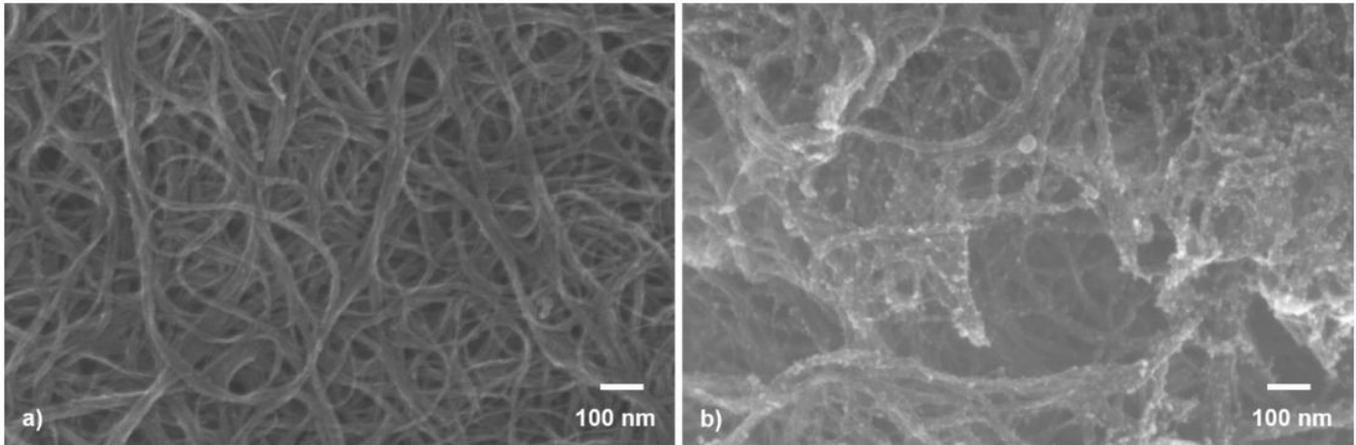


Figure 1

Scheme of the LIFT setup: step 1 – 5 fabrication of the donor substrate by spin coating and step 6 transfer by LIFT of the donor material (SWCNT:SnO<sub>2</sub>) onto the receiver substrate (glass plate with Pt electrodes). Step 1: The donor plate is placed in the spin coater. Step 2 and 3: The quartz plate is coated with a thin film of the triazene polymer (TP). Step 4 and 5: The SWCNT:SnO<sub>2</sub> suspension is spin coated onto the TP/quartz plate. Step 6: The donor and receiver are placed onto a xyz translation stage. The laser beam impinges through the transparent quartz plate, vaporizes the TP which mechanically pushes forward a small portion of the SWCNT:SnO<sub>2</sub> film onto the glass plate with Pt electrodes.

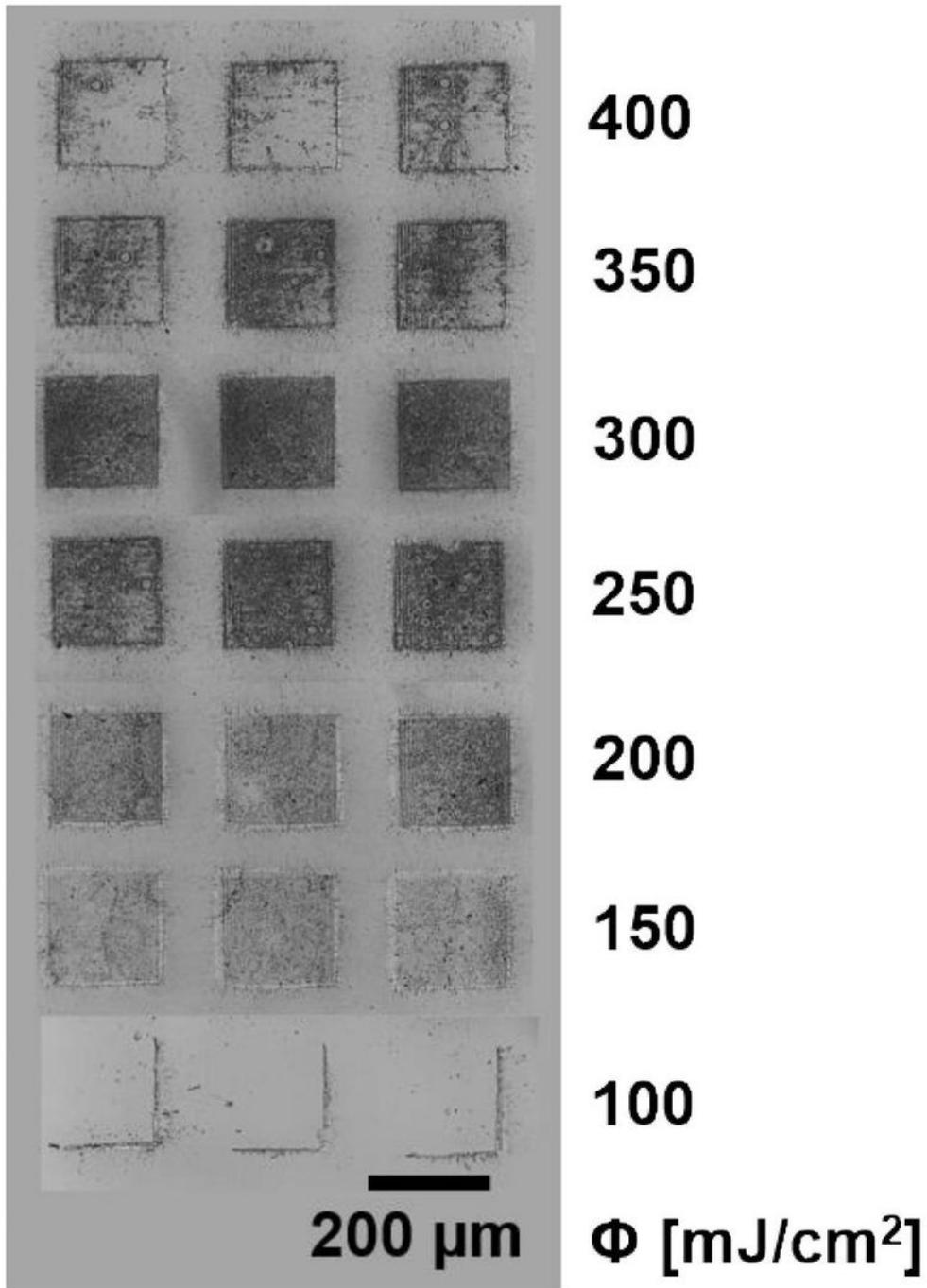
**Fig. 2**



**Figure 2**

Representative SEM images of a) SWCNT and b) SWCNT:SnO<sub>2</sub> donors as fabricated, prior to laser transfer.

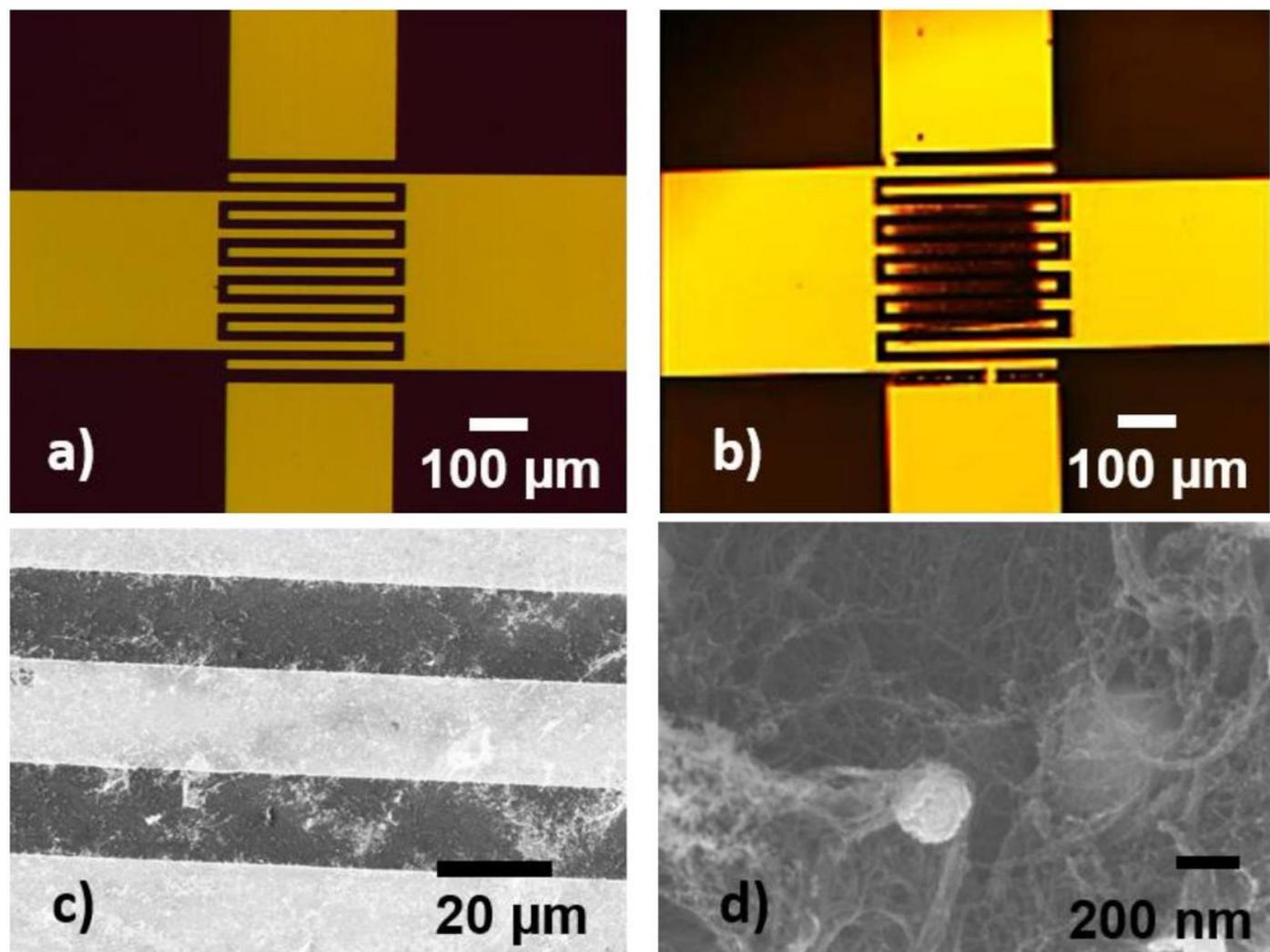
**Fig. 3**



**Figure 3**

SWCNT:SnO<sub>2</sub> microarray transferred by LIFT by keeping in contact the donor and receiver substrates.

**Fig. 4**



**Figure 4**

Optical microscopy images of a) the interdigital electrodes and b) a SWCNT:SnO<sub>2</sub> pixel printed onto the metal electrodes. c) SEM image of SWCNT:SnO<sub>2</sub> pixel transferred by LIFT at 300 mJ/cm<sup>2</sup> laser fluence onto the sensor IDTs, and d) SEM image taken at a higher magnification of a SWCNT:SnO<sub>2</sub> pixel transferred by LIFT at 300 mJ/cm<sup>2</sup> laser fluence onto the sensor IDTs, where the SnO<sub>2</sub> nanoparticles decorating the SWCNTs can be seen.

Figure 5

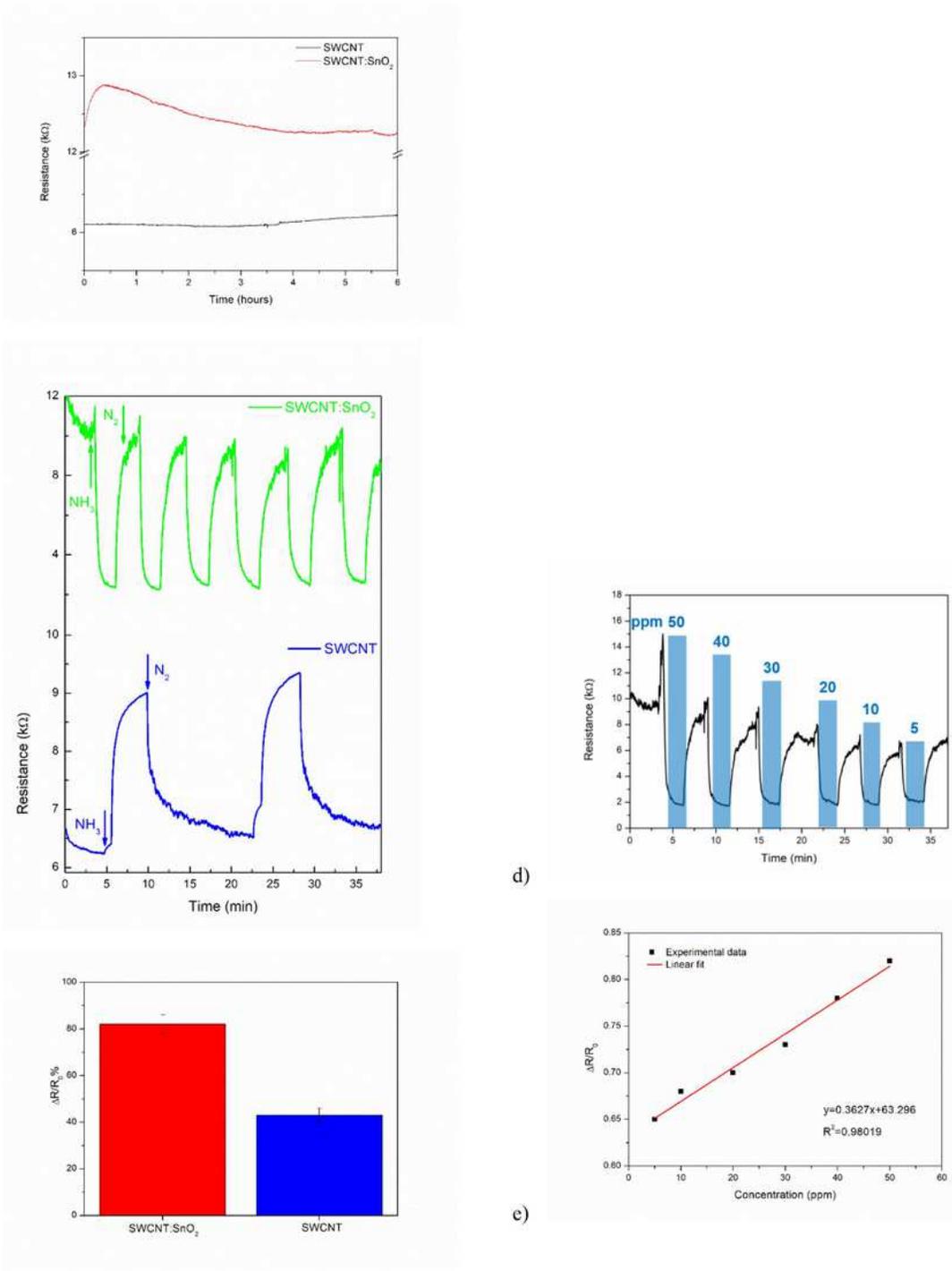


Figure 5

a) Resistance vs time profile for LIFT-ed SWCNT and SWCNT:SnO<sub>2</sub> pixels before exposure to different concentrations of NH<sub>3</sub>. A stable 6 h baseline is depicted. b) Reproducibility of the SWCNT and SWCNT:SnO<sub>2</sub> sensors response printed by LIFT to 50 ppm of NH<sub>3</sub>. c) Comparison of the SWCNT:SnO<sub>2</sub> and SWCNT response to NH<sub>3</sub> at 50 ppm. d) Real-time measurements of a SWCNT:SnO<sub>2</sub> sensor printed

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