# Shape-driven Arrest of Coffee Stain Effect Drives the Fabrication of Carbon-Nanotube-Graphene-Oxide Inks for Printing Embedded Structures and Temperature Sensors: Supporting Information

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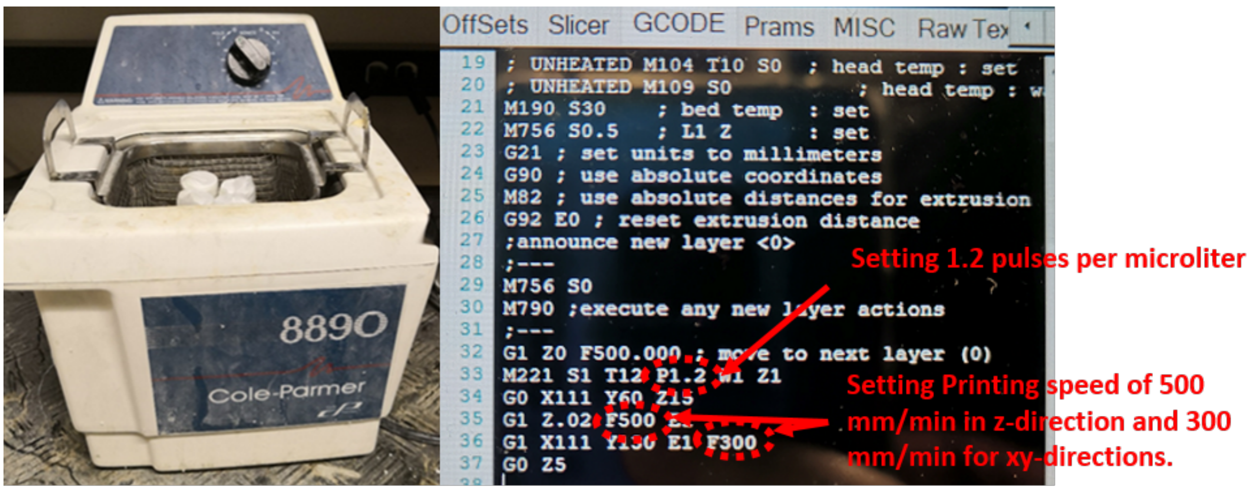
## S.1. Printing

Figure S1(a) shows the sonication of the ink. This sonication process is conducted prior to the printing. Fig. S1(b) shows a sample G-code that was written and loaded in the *Repetrel software* for printing a 70 mm straight line.




(a) (b)

**Figure S1:** (left) Sonication of the ink. (right) The screen capture that is showing the G-code that was written and loaded in the Repetrel software for the printing of a straight line of length 70 mm. In this screen capture, we have identified the printing speed and the pulse rate.

Figure S2 provides the images for more printing results.

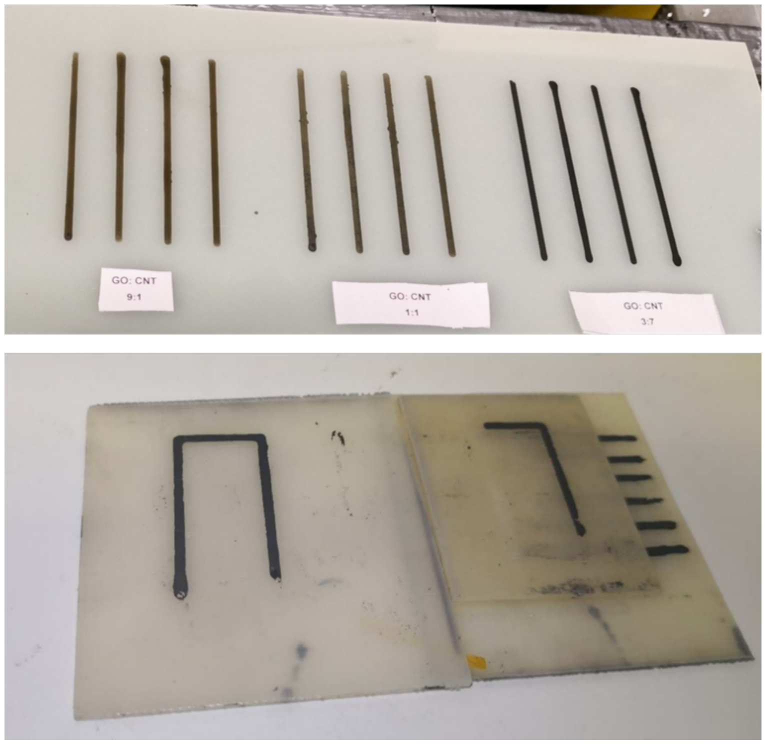



**Figure S2:** (top) Printed straight-line traces with 3 combination of the GO/CNT ink on bare FR4 surface. The left, center, and the right group of lines are printed with GO:CNT=9:1, GO:CNT=1:1, and GO:CNT=3:7 inks, respectively. (bottom) Printed patterns on PDMS-coated FR4 substrate with GO:CNT=3:7 ink.

More printing procedures involving various ink combinations and different substrates have been illustrated in the supplementary videos.

## S.2. Viscosity Measurements of the GO-CNT Ink

In Fig. S3 we provide the picture of the rheometer that was employed to measure the apparent viscosity of the ink under different combinations and conditions [the results are provided in Fig. 2(a,b) in the main paper].

**Figure S3:** Rheometer for ink viscosity measurements.

## S3: Characterization of the Printed Straight-Line Traces

To determine the resistivity $\rho$ of the printed straight-line traces from the measured resistances $R$, the following formula was utilized:

$$\rho = R \times \frac{A}{l} = \frac{R \times t \times w}{l}, \quad \text{(S1)}$$

where $t, w$, and $l$ stand for the thickness, width, and the length of the measured printed traces, respectively. Figure S4 presents experimental setup for measuring the length and the width of the printed straight-line traces.

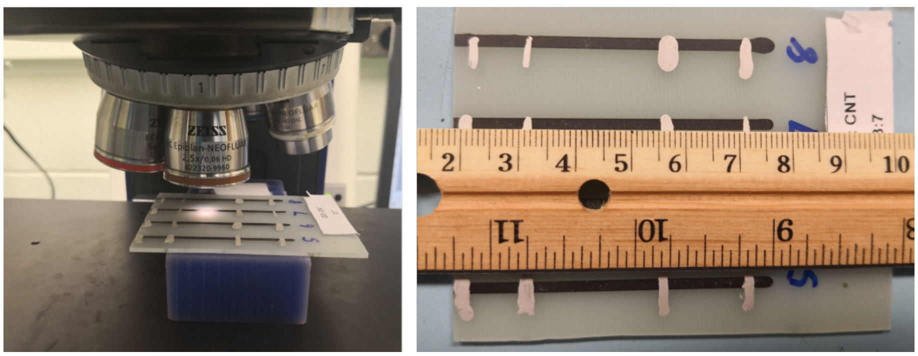



**Figure S4:** Set-up for the width measurements using a microscope (left) and the length (right) measurement using a ruler for the printed straight-line traces.

In Figure S5, we show our profilometery measurements of the thickness of the traces printed on the PDMS-coated FR4 surface. Profilometry was also used to determine the typical coating thickness of the PDMS layer.

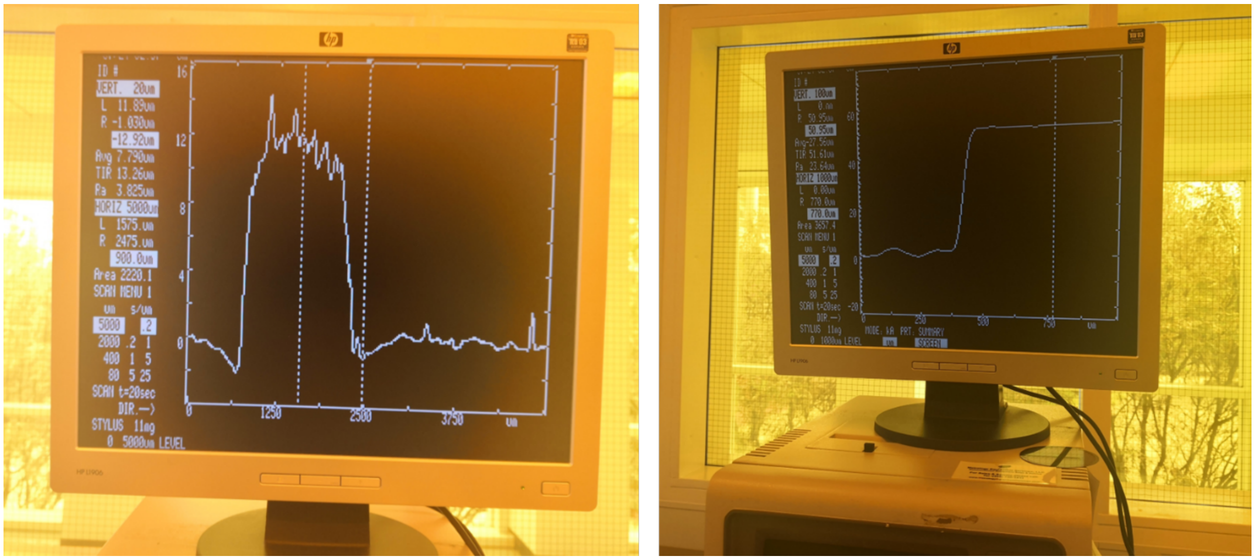


**Figure S5:** Profilometry measurement for the thickness of the coated PDMS layer (left) and the thickness of the GO-CNT ink traces printed on the PDMS-coated FR4 substrate (right).

Surface profilometry measurements were also employed for measuring the thickness of the printed traces (see Fig. S6). It was revealed that increasing the weight fraction of CNT in the ink results in a thicker printed traces with a greater degree of uncertainty. The uncertainty was analyzed using uncertainty propagation [S1] and neglecting the possible correlation.

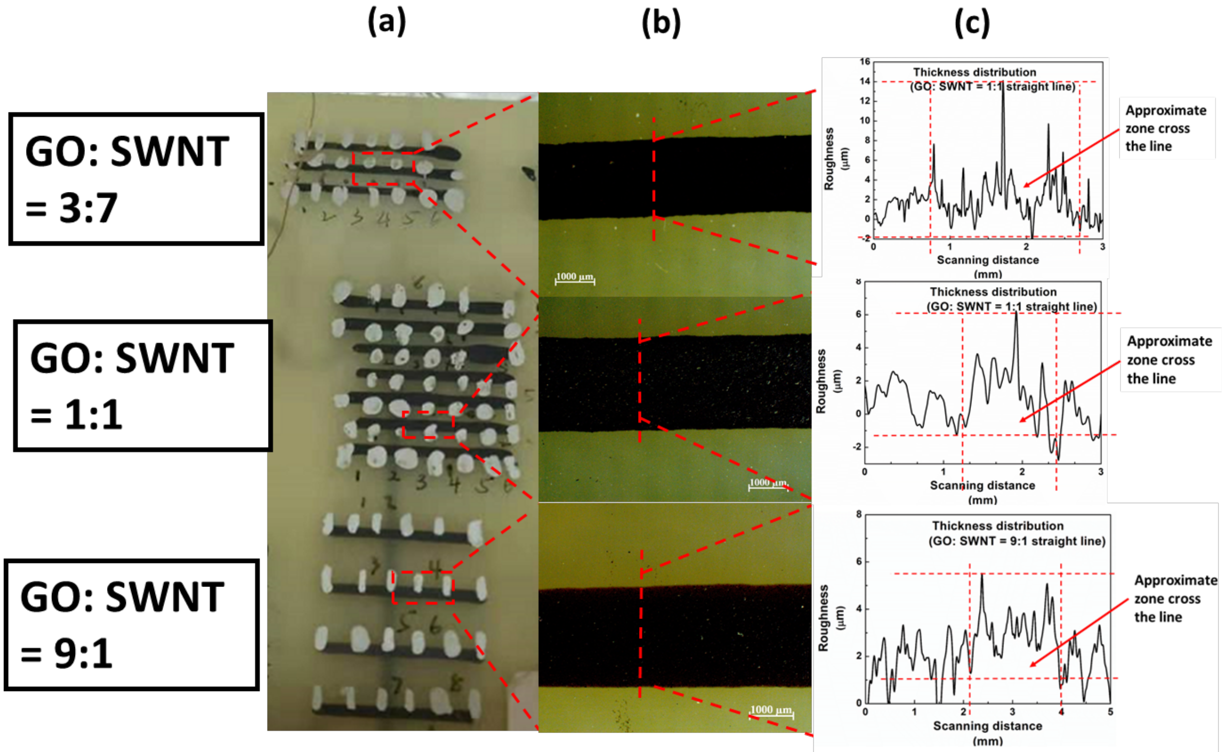



**Figure S6:** Surface profilometry measurements of the printed straight-line traces with (a) GO:CNT=3:7, (b) GO:CNT=1:1, and (c) GO:CNT=9:1.

Additionally, Fig. S7 provides a screenshot of a typical Line Edge Roughness (LER) measurement for straight lines printed by 3 different kinds of ink combinations. This measurement were done by a Matlab based software Line and Contact Edge Roughness Meter (Lacerm).

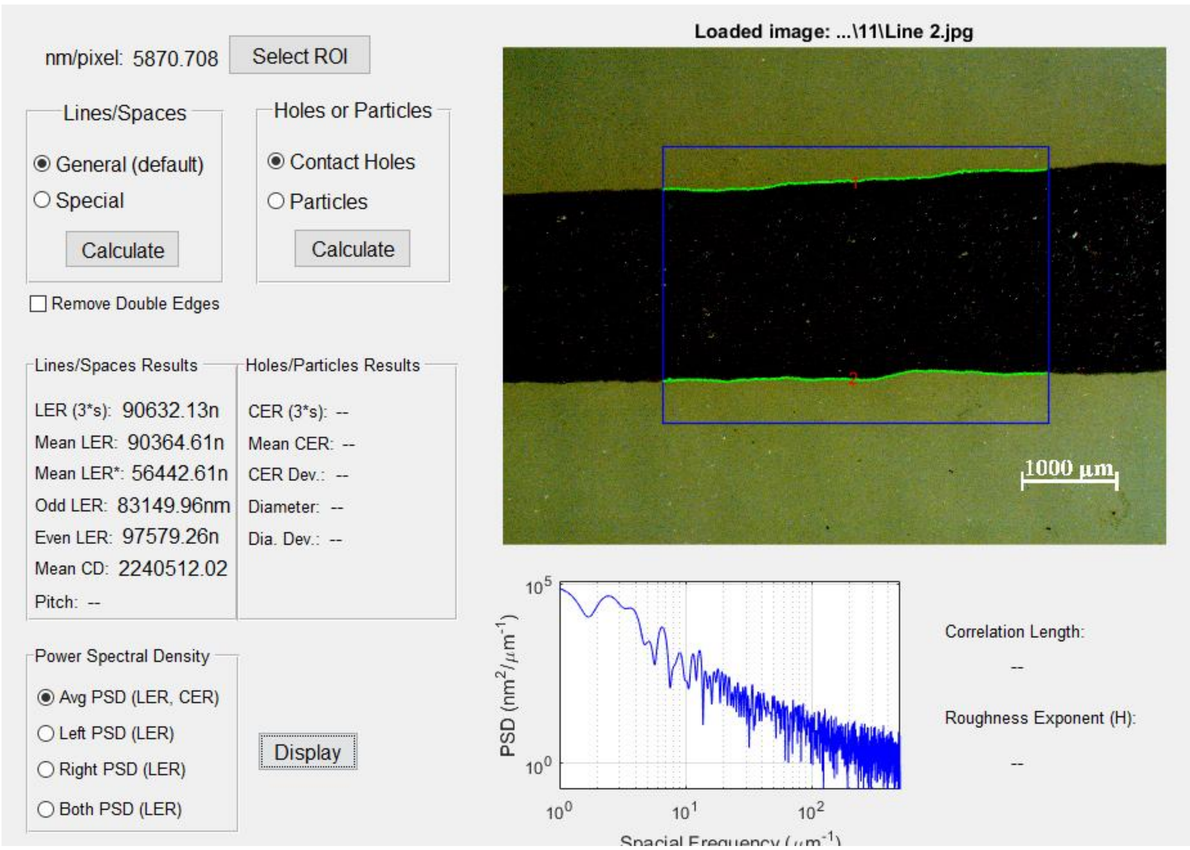



**Figure S7:** A typical Line Edge Roughness measurements screenshot from the software Lacerm. (Shown straight line printed with 5mg/ml CNT:GO = 1:1 ink)

Subsequently, the resistance of the printed straight-line traces was obtained using the 4-probe measurement [see Fig. S8(b)]. The standard deviation of resistivity $\sigma_{\rho_1}$ at temperature $T_1$ can be calculated using the equation S2 and S3.

$$\sigma_{\rho_1} = \left( \left( \frac{\partial \rho}{\partial R_1} \right)^2 \sigma_{R_1}^2 + \left( \frac{\partial \rho}{\partial l_1} \right)^2 \sigma_{l_1}^2 + \left( \frac{\partial \rho}{\partial w_1} \right)^2 \sigma_{w_1}^2 + \left( \frac{\partial \rho}{\partial t_1} \right)^2 \sigma_{t_1}^2 \right)^{\frac{1}{2}} \quad \text{(S2)}$$

$$\sigma_{\rho_1} = \left( \left( \frac{t_1 w_1}{l_1} \right)^2 \sigma_{R_1}^2 + \left( -\frac{R_1 w_1 t_1}{l_1^2} \right)^2 \sigma_{l_1}^2 + \left( \frac{R_1 t_1}{l_1} \right)^2 \sigma_{w_1}^2 + \left( \frac{R_1 w_1}{l_1} \right)^2 \sigma_{t_1}^2 \right)^{\frac{1}{2}} \quad \text{(S3)}$$

Table S1 summarizes the resistance, the dimensions needed to calculate the resistance, as well as the line edge roughness of the straight-line traces printed with the three different inks.

| | **Averaged Width (Unit: mm)** | **Averaged Thickness (Unit: µm)** | **Averaged LER (Unit: µm)** | **Averaged Length (Unit: mm)** | **Averaged Resistance (Unit: Ω)** |
|---|---|---|---|---|---|
| **GO:CNT = 3:7** | $2.06 \pm 0.13$ | $3.99 \pm 0.48$ | $79.36 \pm 42.84$ | $5.67 \pm 0.66$ | $81.70 \pm 9.60$ |
| **GO:CNT = 1:1** | $2.45 \pm 0.20$ | $3.12 \pm 0.32$ | $75.47 \pm 66.30$ | $5.8 \pm 0.71$ | $409.50 \pm 18.37$ |
| **GO:CNT = 9:1** | $2.46 \pm 0.03$ | $3.03 \pm 0.09$ | $71.17 \pm 14.29$ | $5.19 \pm 0.46$ | $(10.13 \pm 2.31)\times10^{6}$ |

**Table S1:** Average values of the resistance of the straight-line traces printed with three different types of inks. The resistances were measured at T~22 ℃. The average values of the different dimensions of the straight lines used to calculate the resistances are also provided. The thickness of each line was obtained from the surface profilometry measurements.

To measure the temperature coefficient of resistance (TCR) of the printed straight-line traces, we built a flexible probe system for exploring the relationship between resistance of the printed traces and the substrate temperature. In Figure S8, we present a 4-probe system with a hotplate to measure the TCR of a printed trace (printed using GO: CNT = 3: 7 ink). Figure S8 provides the experimental schematic and experimental setup, while Figure S9 provides the V-I plot under different surface temperatures obtained using the 4-probe measurement system.

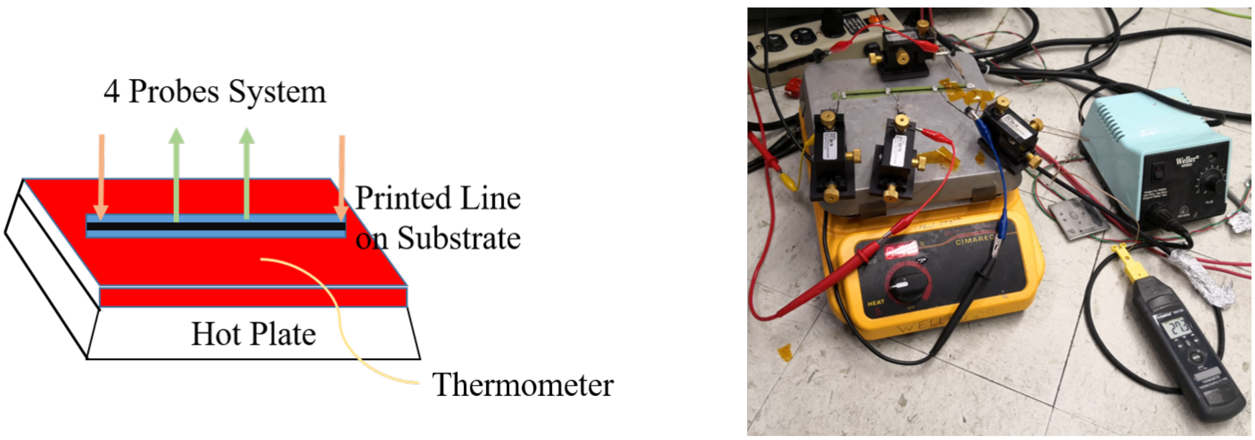



**Figure S8:** 4-Probe measurements for straight-line traces lines printed with GO: CNT = 3:7 ink on a hotplate whose temperature can be controlled. (Left) Schematic. (Right) Experimental Setup. The same four-probe measurement has been used to quantify the resistance of the straight-line traces printed with GO: CNT = 3:7, 1:1, 9:1 inks at a fixed temperature (22 ℃) (results are provided in Table S1).

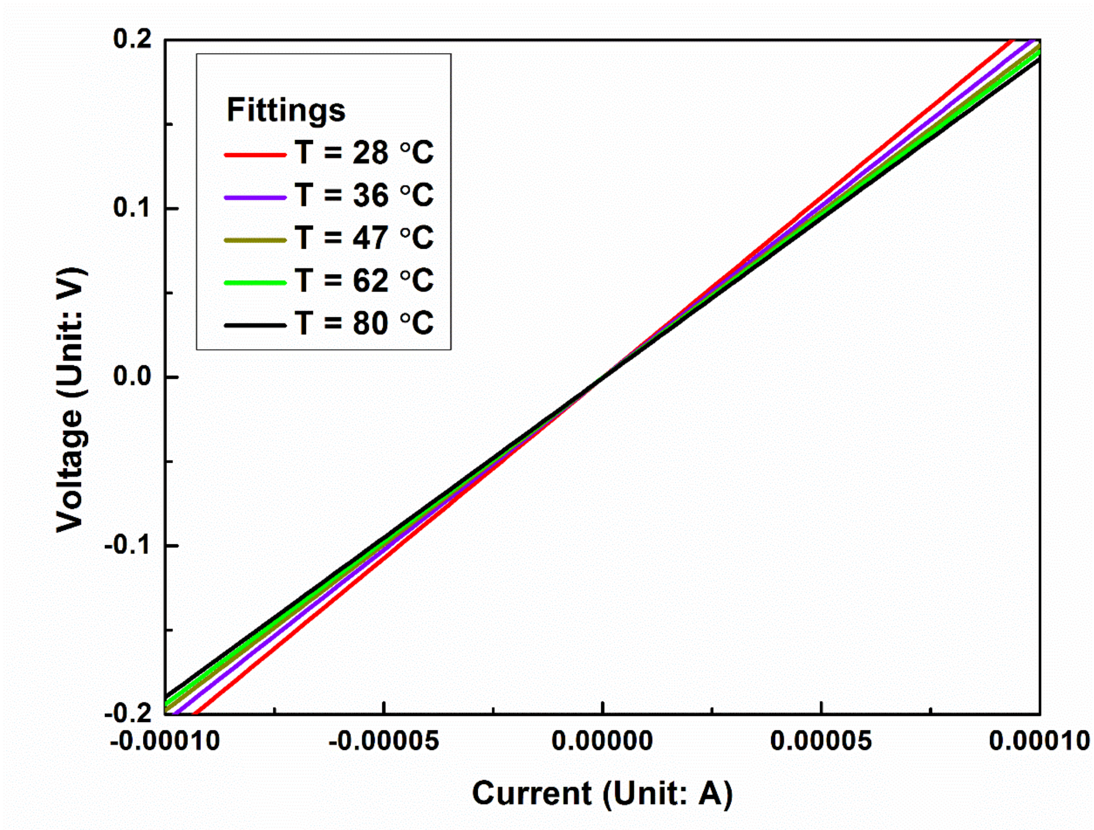



**Figure S9:** V-I plot at surface temperature of 1). T = 28 ℃ , R = 2138 Ω; 2) T = 36 ℃ , R = 2038 Ω; 3). T = 47 ℃ , R = 1970 Ω; 4). T = 62 ℃ , R = 1934 Ω; 5). T = 80 ℃ , R = 1892 Ω.

Employment of a coating is sometimes necessary to create a conductive trace for the SEM. However, the coating material (either gold or carbon coating) has a relatively larger particle size compared to the CNTs, which made the CNTs non-visible under SEM observation. On the other hand, our printed lines show a reasonable conductivity, which is sufficient for the SEM observation. Therefore, for the specimen prepared for the SEM analysis [results shown in Figs. 3(b-d) in the main paper], no conductive coating layer was added (see Fig. S10).

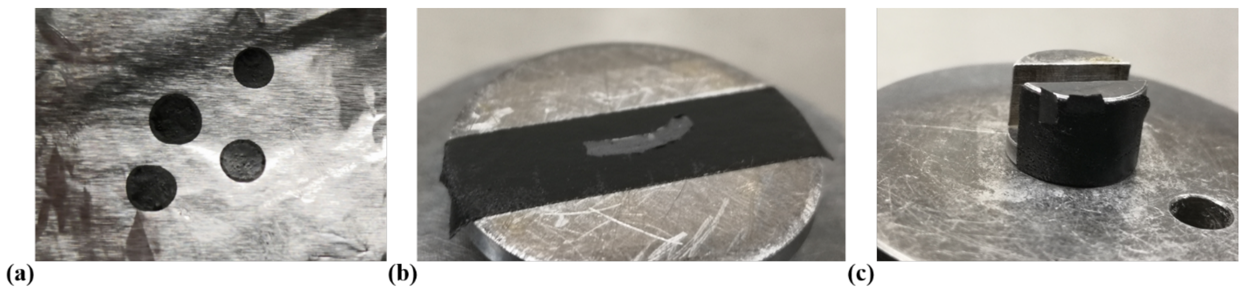



**Figure S10:** SEM specimen preparation without additional coating. (a) Ink droplets on aluminum foil. (b) Specimen for obtaining top-view SEM. (c) Specimen for obtaining cross-sectional SEM.

## S4: Drop evaporation experiments

Micropipettes were employed for droplet experiments. A DragonLab Micropipette was set at 20 μL to ensure the volume of each deposited droplet was almost identical. Digital camera Nikon Coolpix L830 was applied for obtaining the images of the equilibrated liquid droplet. A tripod was used to fix the position of the camera, and a mark was made on the location of the substrate placement. In Figure S11, we show (a) the micropipette applied for droplet deposition, (b) set up for capturing the optical image of the evaporating droplet, and (c) set up for the profilometry measurements using the Tencor P-1 long scan profilometer.


**Figure S11:** (a) Micropipette for droplet volume control; (b) set up for capturing the optical image of the evaporating droplet, and (c) set up for the profilometery measurement (using Tencor P-1 long scan profilometer) for quantifying the thickness variation of the deposits resulting from the evaporation of the CNT-GO-laden or pure GO-laden drops.

The drop evaporation experiments for GO: CNT inks were conducted under ambient temperature. Microscope images were captured every 5 minutes until the drop had fully evaporated. Figures S12 and S13 present the detailed experimental recordings for the droplet evaporation experiments.

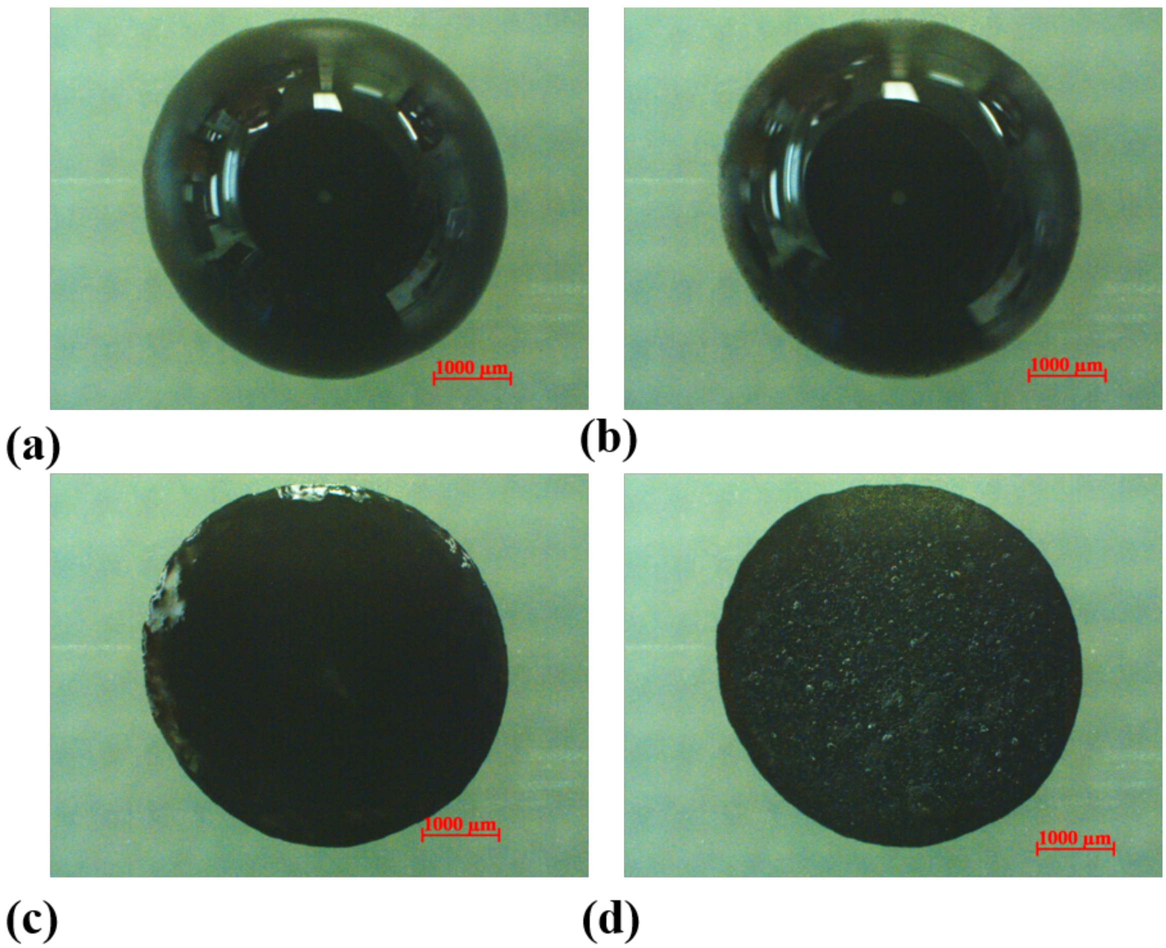



**Figure S12:** Pictures showing the evaporating drop (and the corresponding post-evaporation deposits) for a drop of GO: CNT = 3:7 ink at (a) 0 min (i.e., immediately) after the drop deposition; (b) 15 minutes after the drop deposition; (c) 30 minutes after the drop deposition; (d) 45 minutes after the drop deposition (case when the drop is fully evaporated).

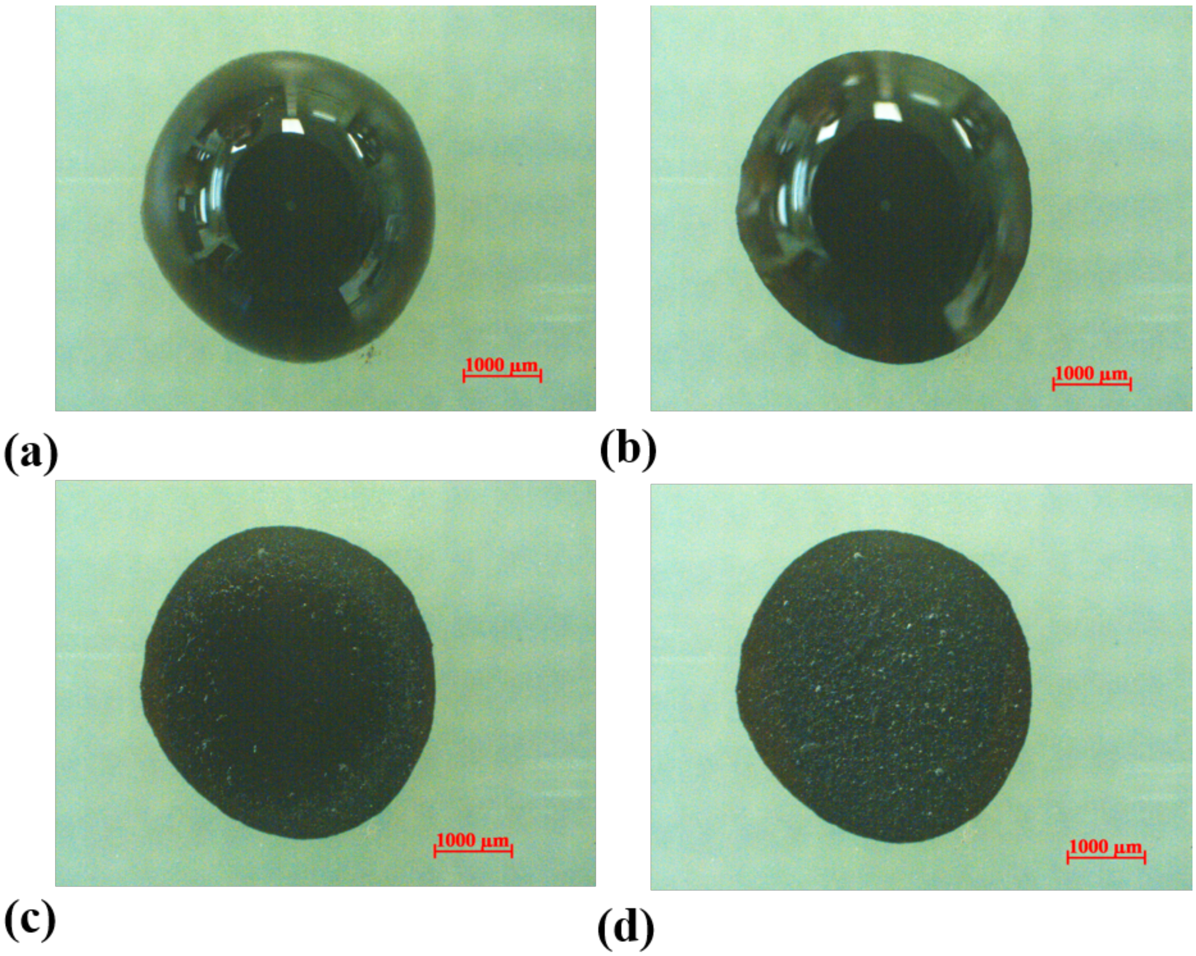



**Figure S13:** Pictures showing the evaporating drop (and the corresponding post-evaporation deposits) for a drop of GO: CNT = 9:1 ink at (a) 0 min (i.e., immediately) after the drop deposition; (b) 15 minutes after the drop deposition; (c) 30 minutes after the drop deposition; (d) 45 minutes after the drop deposition (case when the drop is fully evaporated).

## S5: Properties of the Printed Patterns

Fig. S14 provides a schematic for the description of the dimension of printed serpentine (sensor-like) patterns. Figs. S15 and S16 provide the surface profilometry measurements (for the thickness and the edge roughness) and the optical imaging (for the width) of the different sections of the sensor-like patterns printed with the GO:CNT=1:1 and GO:CNT=3:7 inks. From the optical images shown in Figs. S15 and Figs. S16, we can find that the width of the patterns printed with the GO:CNT = 1:1 is more uniform.

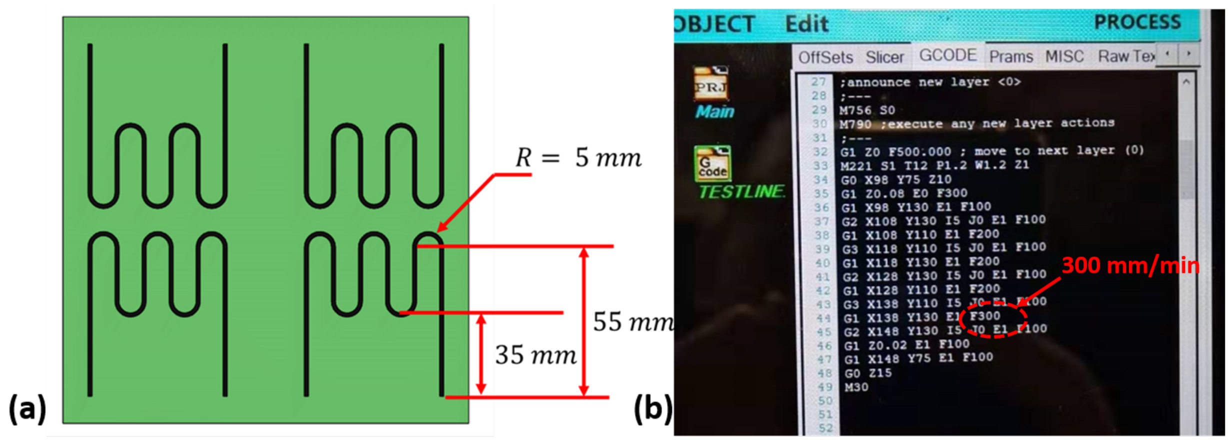



**Figure S14:** (a) Schematics for newly printed serpentine patterns to validate the printability and reproducibility; (b). G-codes applied to print those patterns (Minor differences among different patterns, with printing speed ranging from 100 mm/min to 300 mm/min)

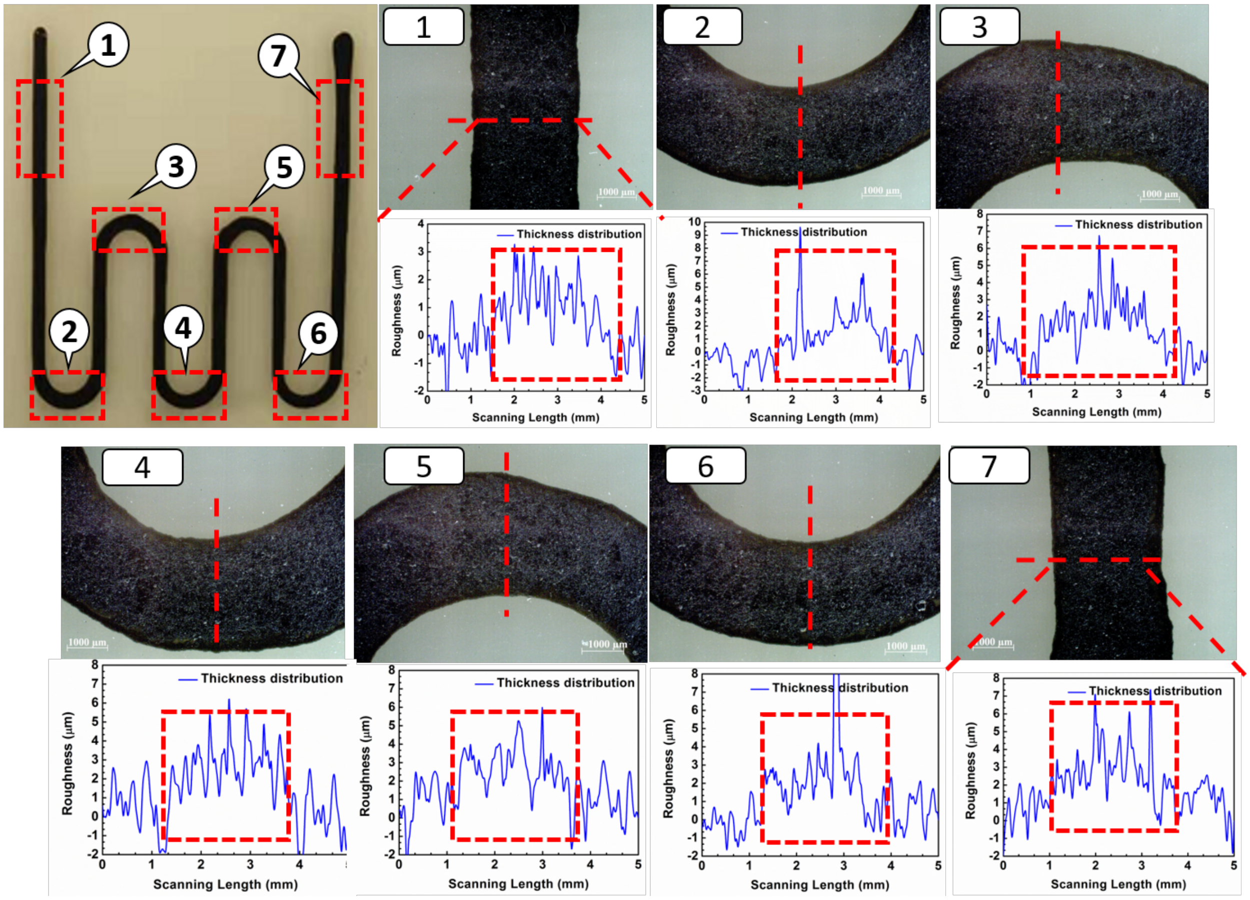



**Figure S15:** Optical measurements (showing the width) and the surface profilometry measurements (showing the thickness and the edge roughness) of the different sections (identified in the leftmost image) of the serpentine trace printed with GO:CNT=1:1 ink having a concentration of 7.5 mg/ml.

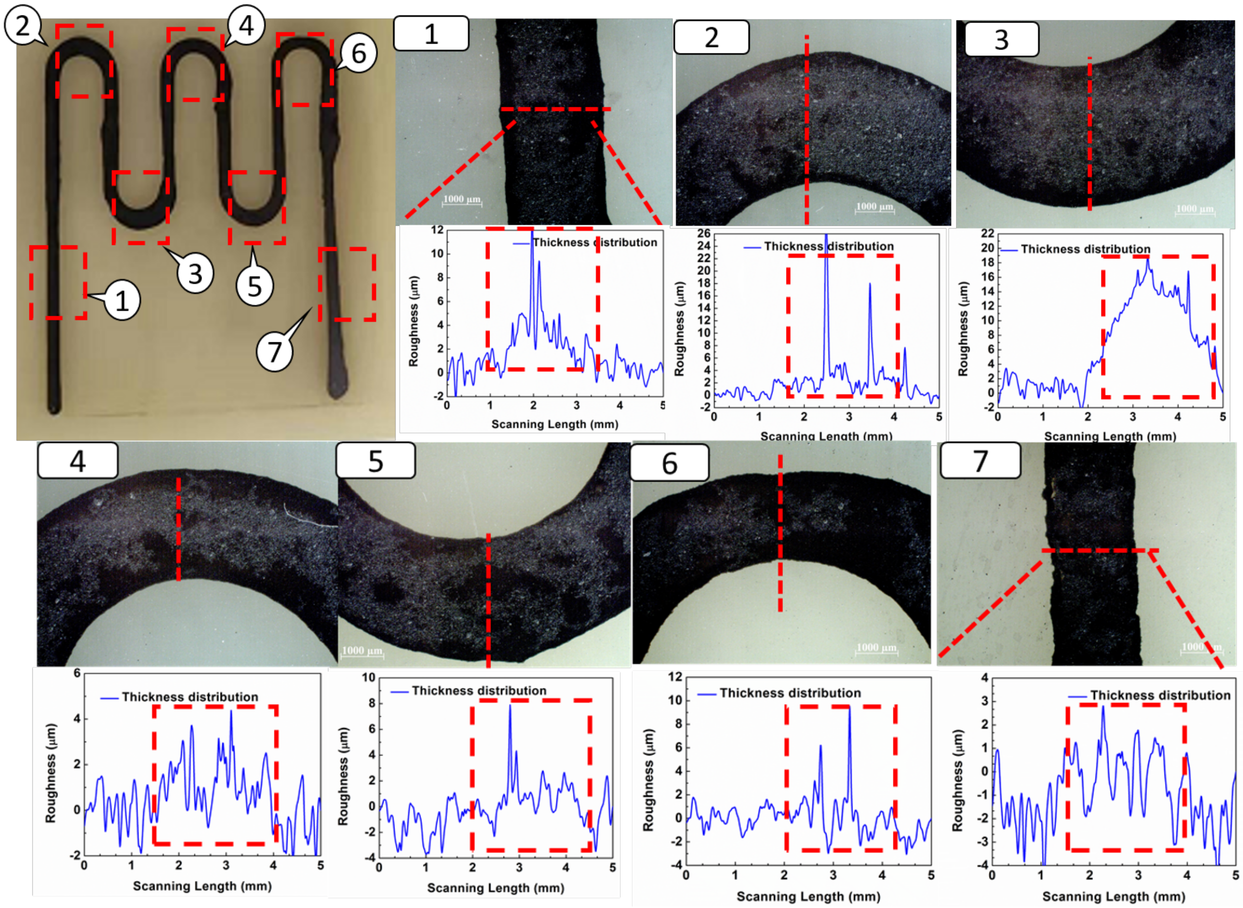



**Figure S16:** Optical measurements (showing the width) and the surface profilometry measurements (showing the thickness and the edge roughness) of the different sections (identified in the leftmost image) of the serpentine trace printed with GO:CNT=3:7 ink having a concentration of 7.5 mg/ml.

Figs. S17 and S18 provide the surface profilometry measurements (for the thickness and the edge roughness) and the optical imaging (for the width) of the different sections of the spiral patterns printed with the GO:CNT=1:1 and GO:CNT=3:7 inks. From the microscopic images shown in Figs S17 and Figs. S18, it can be observed that here too that patterns printed with GO: CNT = 1:1 ink is more uniform than the patterns printed with GO:CNT = 3:7 ink.

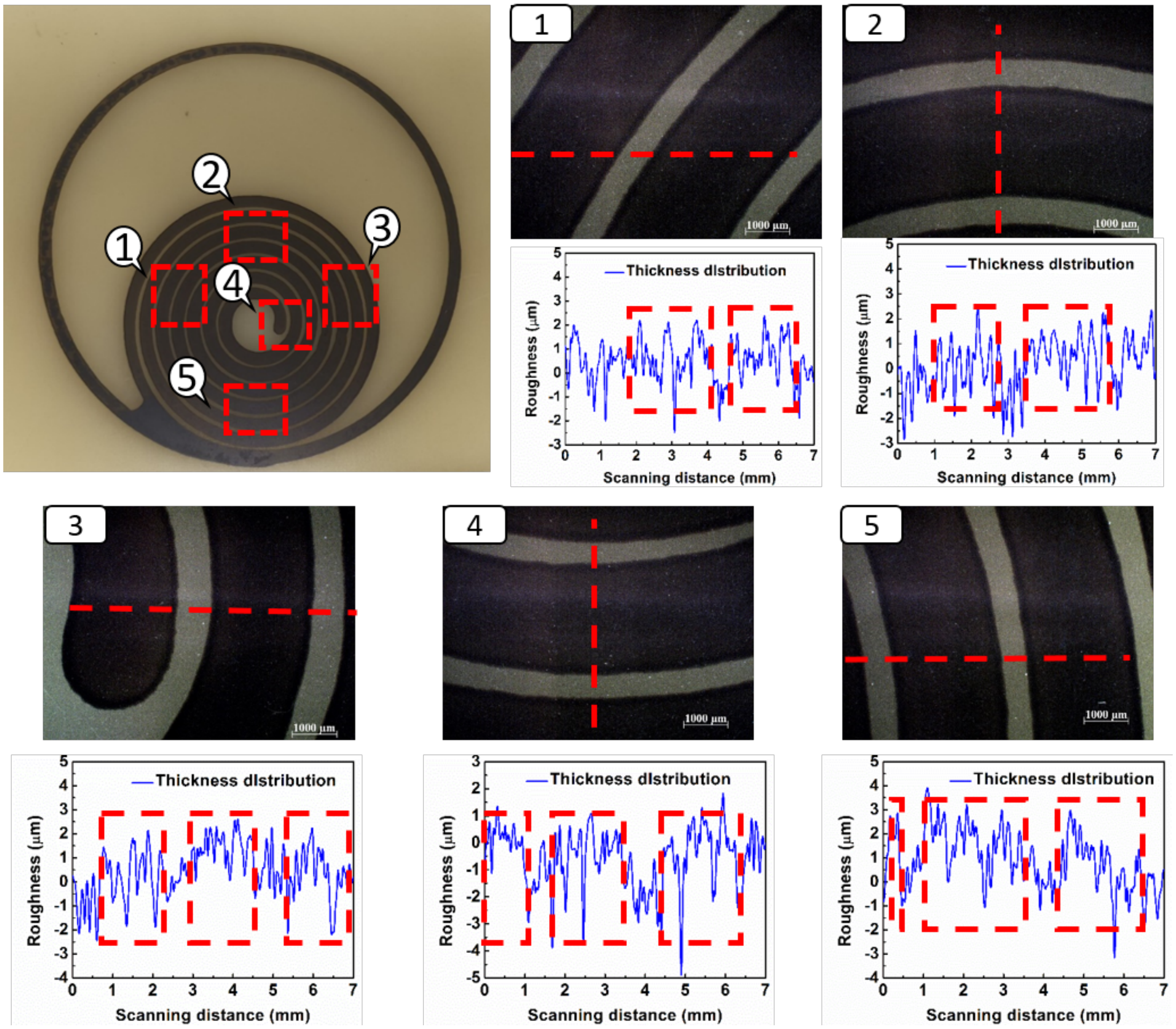



**Figure S17:** Optical measurements (showing the width) and the surface profilometry measurements (showing the thickness and the edge roughness) of the different sections (identified in the leftmost image) of the spiral pattern printed with GO:CNT=1:1 ink having a concentration of 5.5 mg/ml. In the figures showing the thickness distributions, the printed trace area was highlighted with rectangular boxes.

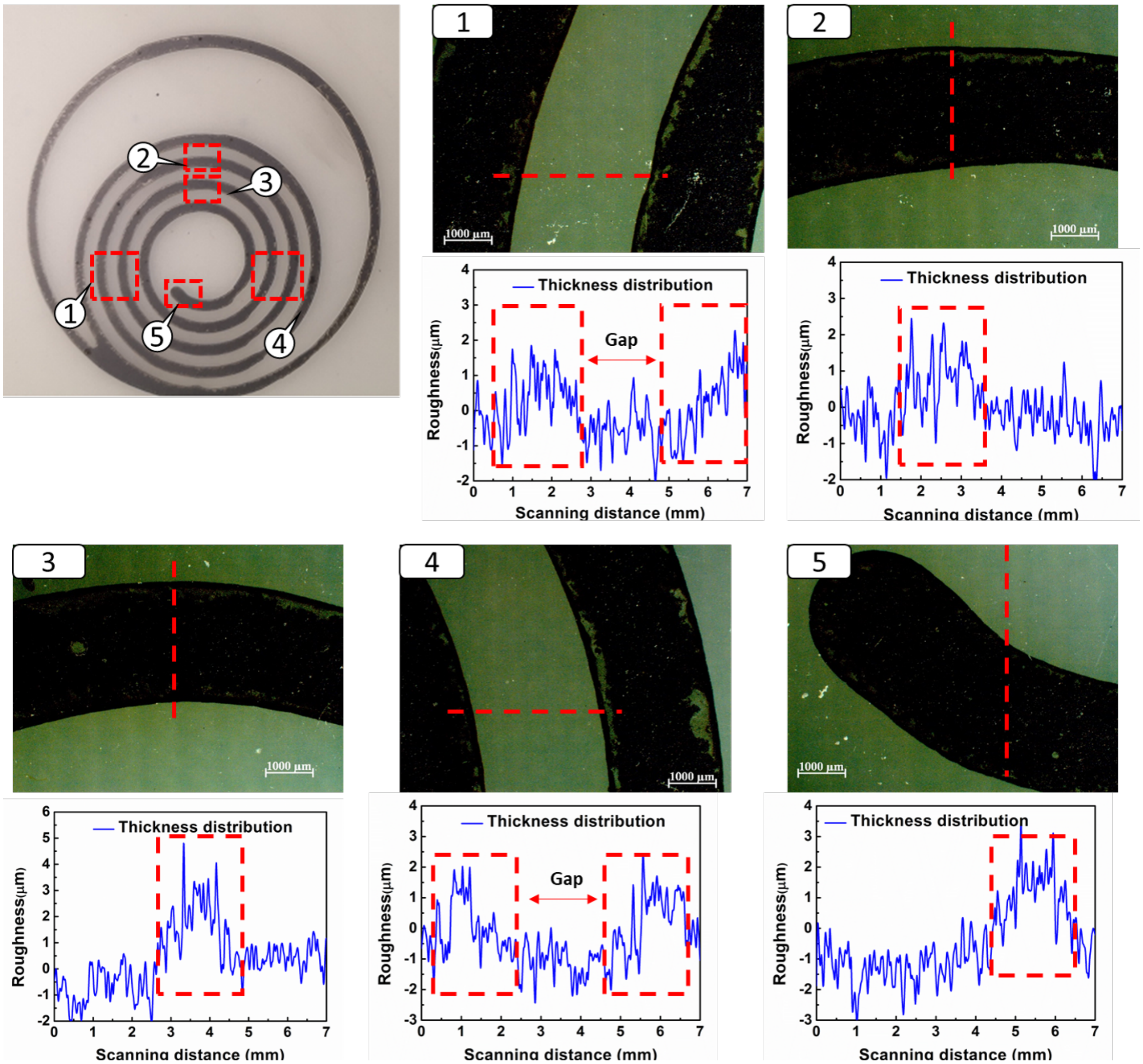



**Figure S18:** Optical measurements (showing the width) and the surface profilometry measurements (showing the thickness and the edge roughness) of the different sections (identified in the leftmost image) of the spiral pattern printed with GO:CNT=3:7 ink having a concentration of 5.5 mg/ml. In the figures showing the thickness distributions, the printed trace area was highlighted with rectangular boxes.

Finally, based on the fact that resistance of the printed patterns is significantly larger than contact resistance, the TCR measurement for printed, sensor-like pattern [see the right of Fig. S19(a)] employed a 2-probe multi-meter. IR thermometer and thermocouples were applied to determine the substrate surface temperature. The experimental setup and the IR thermometer are shown in the Figure S19(b) and S19(c), respectively. Fig. S20 shows the Fluke 23 Series II meter that was employed for the 2-point current measurement.

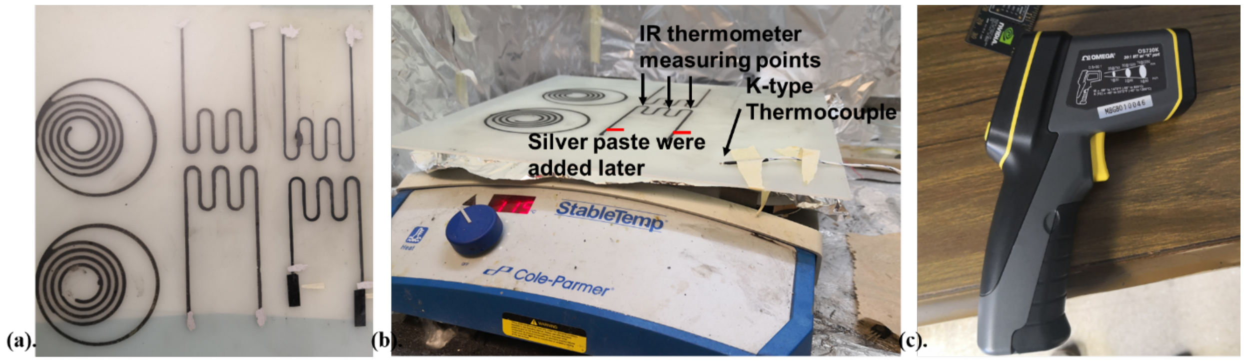



**Figure S19:** TCR measurements for printed sensor-like patterns with GO: CNT = 1:1 ink. (a-right) Printed sensor patterns. (b) Experimental setup. (c) IR thermometer.


**Figure S20:** Fluke 23 Series II meter, which applied for all the 2-point resistance measurements in this experimental study.

**Supplementary Videos**

**Movie S1.** Printing straight-line traces on a flat surface with GO: CNT = 3:7 ink

**Movie S2.** Printing straight-line traces on a flat surface with GO: CNT = 1:1 ink

**Movie S3.** Printing straight-line traces on a flat surface with GO: CNT = 9:1 ink

**Movie S4**. Printing sensor pattern on a flat surface with GO: CNT = 3:7 ink

**Movie S5**. Printing straight-line traces (along the direction of curvature) on a curved surface with GO: CNT = 9:1 ink

**Movie S6**. Printing straight-line traces (perpendicular to the direction of curvature) on a curved surface with GO: CNT = 9:1 ink

**Movie S7**. Printing of spiral pattern on a flat surface with GO: CNT = 1：1 ink

**References**

[S1] Coleman, H. W.; Steck, W. G. Experimentation and Uncertainty Analysis for Engineers, Third Edition, Wiley, 2009.