Printing Ultrasensitive Artificially Intelligent Sensors Array with a Single Self-Propelled Droplet Containing Nanoparticles

Ekhas Homede, Mohammad Abo-Jabal, Radu Ionescu, and Hossam Haick*

The fabrication and implementation of artificially intelligent sensor arrays has faced serious technical and/or cost-effectiveness challenges. Here, a new printing method is presented to produce a fully functional array of sensors based on monolayer-capped gold nanoparticles. The proposed printing technique is based on the so-called self-propelled antipinning ink droplet, from which evaporative deposition takes place along the path of motion. By applying actuating forces, different deposition line patterns with different thicknesses and morphology from a single droplet are generated. The functionality of the produced sensors is demonstrated by their ability to detect different representative volatile organic compounds (VOCs) belonging to different chemical families, including alcohols, alkanes, ethers, and aromatics, and under extremely different humidity levels resembling those encountered in real-world conditions. The results show that the sensors exhibit ultrasensitive sensing features, with an ability to detect and differentiate between different VOCs at low ppb levels. Additionally, the results show that the sensors are able to accurately predict VOC concentrations, viz. enable quantification capabilities, while nevertheless being inexpensive, do not need complicated and expensive printing equipment and prepatternning processes, allow low voltage operation, and provide a platform for multifunctional applications.

1. Introduction

Artificially intelligent sensor arrays for the detection of a wide range of chemical and biological compounds in different fields have an important role to play in the sensors technology. Artifically intelligent sensor arrays mimic the human olfactory system in identifying complex gas mixtures. Each sensor in the array has medium to high affinity toward specific (pattern of) component(s) in the mixture. The combined responses of the sensors in the array is analyzed by means of pattern recognition algorithms and classification techniques to yield fingerprints of the targeted analytes.

An artificially intelligent sensor arrays based on nanomaterials have the potential to target real-world sensing applications by having extremely low detection limits (ppb), a wide dynamic range, and tolerance to a range of chemical backgrounds, while nevertheless being small in size and working at room temperature operation, low cost, etc. This is because nanomaterials can increase the active surface area of the sensors and generate new interfaces, thereby improving sensitivity, response and recovery times. Sensor arrays using nanomaterials include field effect transistors based on single-walled carbon nanotubes (CNTs) or nanowires of various materials, and chemiresisitors based on films of monolayer-capped metal nanoparticles or random networks of single-walled CNTs amongst others.

Several techniques have been used so far in fabrication of nanomaterial-based sensors, including: (i) drop casting, where a droplet containing a specific type of nanomaterial suspended into an organic solvent is deposited onto electrodes and followed by natural evaporation of the solvent; (ii) layer-by-layer, where the electrodes are repeatedly exposed to a solution of nanomaterials for several cycles to obtain the desired film thickness; (iii) spray coating, where droplets of nanomaterials are sprayed onto a surface to form a coating layer from which the solvent evaporates, and the nanomaterial thus gets deposited onto the electrodes; (iv) flow-assisted deposition, where microfluidic channels enable directional flow for the deposition of a nanomaterial suspension onto a solid state surface; (v) deposition by chemical interaction, where the interactions between the nanomaterials and the substrate, which promote the corresponding deposition of the nanomaterials, strongly depend on the chemical functionality of the surface; (vi) Langmuir–Blodgett technique, where a surfactant is used to generate a layer with aligned nanomaterials on a surface of a liquid, from which the nanomaterial layer gets transferred to a planar substrate; (vii) blown-bubble technique, where the
expansion of a polymer suspension of nanomaterials (e.g., Si nanowires[49,50]) is blown as a bubble that is transferred to a substrate.[51] (vii) electric field directed deposition, where alternating the voltage between adjacent electrodes allows polarization and alignment of the nanomaterials before their deposition on a substrate,[52] and (viii) contact transfer technique, where a shear force is generated by mechanical sliding of two solid surfaces along each other - one surface being the nanomaterials growth substrate and the other surface being the device.[53]

For many sensor array applications, the need to achieve large patterning areas covered with thin films at relatively low cost has led to extensive efforts to adapt the ink printing methods, such as ink-jet printing, screen printing, and contact printing.[54,55] In many cases, the droplets used in the printing process suffered from dynamic coffee-ring regime,[56] i.e., deposition of most of the nanomaterials takes place on the two outer ridges of the droplet, leaving very small amount of material deposited in between, leading to noncontinuous morphology of the film.[57] Printing techniques are also being challenged by the need for large and heavy instrumentation, special adaptations for different types of nanomaterial inks, alignment between the nozzle and the substrate, and the need for special printing heads with multiple tips to print a number of sensors simultaneously.

We report here on the fabrication of a fully functional array of sensors by means of a novel printing technique, avoiding the need for highly sophisticated instruments and/or specific kinds of inks. This method is based on the self-propelled antipinning ink droplet, from which deposition by evaporation takes place along the motion path.[57] By applying actuating forces, e.g., gravity, different deposition line patterns from a single droplet can be made; this approach allows the production of distinctive and controllable deposition patterns. Films with a thickness gradient along the actuation path of the droplet can be created, which in turn make them attractive for producing functionally graded devices.[58] As a demonstration of this concept, we will focus this paper on the fabrication of an array of chemiresistive films of monolayer-capped gold nanoparticles (AuNPs). Combining the printing ability gained from our new printing technique with the power of AuNP-based sensors, we will show the fabrication of a fully functional cross-reactive sensors array from a single droplet containing AuNPs. The functionality of the resulting sensors array is demonstrated by its ability to detect different representative volatile organic compounds (VOCs) from different chemical families, including alcohols, alkanes, ethers, and aromatics, under highly variable humidity conditions, from which we can also estimate their concentrations.

2. Results and Discussion

Figure 1A illustrates schematically the experimental work and analysis procedures used in the investigations. Three different solutions of gold nanoparticles (5.1–7.2 nm in diameter) capped with 1-hexanethiol (C6), 1-dodecanethiol (C12), or 1-ocatadecanethiol (C20) were synthesized and characterized as reported earlier[19,59] and presented in Section I & Figure S1 (Supporting Information). This series of different lengths of ligands was chosen to carry out a systematic examination of their effects on the interaction with targeted VOCs. Actuating a single droplet of AuNPs ink, made of a binary mixture of solvents (toluene and nonane) over interdigitated Ti/Au (20/380 nm) microelectrodes patterned on Si/SiO2 wafer, with 1.2 mm interelectrode spacing, allowed the deposition of distinctive AuNP patterns during solvent evaporation over the microelectrodes along the actuation path.[56] Adjusting the droplet velocity by tilting at different angles provided controllability over the droplet shape during its travel, thereby producing different deposition patterns from the trail (see Movie S1, Supporting Information).

Four different flow regimes were obtained from the motion of these droplets (Figure 1B), from which four different deposition patterns were emerged: (a) dynamic coffee-ring pattern; (b) microrivulet (µ-R) deposition pattern; (c) macrorivulet deposition pattern; and (d) spreading (SP) droplet deposition pattern.[58] Details about the patterns, their geometrical characteristics, and flow mechanisms can be found in our previous publication.[56] Three of these four patterns were stable and well-controllable. The fourth pattern (macrorivulet) was unstable at the droplet receding contact line, viz. produce non-continuous and noncontrollable deposition pattern behind the droplet path. Therefore, this deposition pattern was excluded from the study. The dynamic coffee-ring regime gave a controlled characteristic double-ridge pattern, but the morphology of the deposited nanomaterials in between the two ridges was not continuous and/or uniform and/or reproducible; therefore it was excluded also from the study.

The sensing behavior of the sensors array achieved by each of these deposition techniques was further investigated. The two series of sensor arrays were exposed to different types of VOCs (Table 1) at 0%, 30%, and 90% relative humidity (RH). The results were analyzed statistically to evaluate their discrimination and quantification power of VOC concentrations, and to test the possibility of integrating them in self-learning sensing systems that can work under real confounding factors.

The sensing mechanism of the VOCs by the AuNP-based sensors relates to molecular interactions occurring between the ligands capping the AuNPs and the VOCs. There are a number of parameters—core size and shape, conjunction length, side chain nature, and intermolecular forces (Van der Waals forces)—that can individually or cooperatively dominate the organization of the system, and as a consequence influence charge transport. For a further explanation of the electron transport mechanism through the thin film-sensing layer, see Section II in the Supporting Information.

Figure 2a shows the two different deposition patterns obtained on the circular interdigitated microelectrodes made of gold (Experimental Section). Once the droplet was actuated, the solvent evaporated, leaving different thicknesses of the deposited AuNPs layer along the droplet trail. As a consequence, the “effective” concentration of the AuNPs inside the droplet increased depending on the extent of evaporation. An increase in the layer thickness occurred toward the head of the droplet. Atomic force microscopy (AFM) was used to investigate the thickness and morphology differences along the trail of the AuNPs droplet for both deposition patterns (see the Experimental Section). Figure 2b shows increased thicknesses along the µ-rivulet deposition pattern from ≈80 to ≈300 nm over a
path of ≈0.5 mm. For the SP, the increase in the thickness was from ≈100 to ≈400 µm over a path of ≈0.45 mm. Differences in layer thicknesses can be attributed to differences in the flow dynamics between the two sliding droplets. The droplet from which the µ-rivulet emerged is more dynamic on its surface and is also unpinned to it because of the binary composition of the solvent (toluene and nonane) inducing solutal Marangoni vortices inside. This lowers the forces between the nanoparticles inside the droplet and the surface, but evaporation of the solvent also increases the concentration of the AuNPs. As a consequence they gradually deposit on the surface until all the solvent has evaporated. On the other hand, SP was produced from a monosolvent droplet of AuNPs suspended into toluene. This droplet is less dynamic when running down on an inclined surface. Furthermore toluene has a higher vapor pressure than nonane, and, therefore, a droplet with toluene evaporates faster than from a toluene and nonane mixture. As a result, higher shear forces operate on the droplet, leading the AuNPs to deposit rapidly and form a thicker layer.

Using these two deposition modes, six types of sensors were fabricated, characterized by their deposition pattern and the ligand type capping the AuNPs (Table 2). Sensors from different locations along the droplets trails were analyzed for both deposition patterns. They were exposed to eight types of VOCs which belonged to different material families. Table 1 shows the VOCs list and the physical properties of each of them.
Exposure of the sensors to these VOCs was carried at the three humidity levels (0%, 30% and 90% RH). The effect of humidity on sensing responses remains one of the paramount issues in the field of chemical gas sensors, because most gas sensing applications are carried out under atmospheric conditions with moderate to high humidity levels. 30% RH was chosen as a representative value of moderate humidity, and 90% as a significantly high level. The sensors were exposed to six increasing concentrations (100, 200, 400, 600, 800, and 1000 ppb) of each VOC at all three humidity levels. All the sensors responded rapidly and reproducibly when exposed to this range of VOCs. The response of some sensors increased monotonically with VOC concentration.

**Table 1.** Physical properties of the VOCs used for the exposure experiments.

| VOC       | Polarity     | Chemical family | Formula      | Molecular mass [g mol⁻¹] | Vapor pressure [kpa @20 °C] | Dipole moment [debye] | Dielectric constant | Density [g cm⁻³] |
|-----------|--------------|-----------------|--------------|---------------------------|-----------------------------|-----------------------|---------------------|------------------|
| 1-Octanol | Polar        | Alcohols        | CH₃(CH₂)₇–OH | 130.2                     | 0.114                       | 1.76                  | 10.3                | 0.824            |
| 1-Hexanol | Polar        | Alcohols        | CH₃(CH₂)₅–OH | 102.2                     | 0.133                       | 1.80                  | 13.3                | 0.813            |
| Ethanol   | Polar        | Alcohols        | CH₃CH₂–OH    | 46.07                     | 0.95                        | 1.69                  | 24.3                | 0.789            |
| Decane    | Nonpolar     | Alkanes         | CH₃(CH₂)₉CH₃ | 142.3                     | 1.58                        | 0                     | 1.98                | 0.73             |
| Hexane    | Nonpolar     | Alkanes         | CH₃(CH₂)₉CH₃ | 86.23                     | 1.76                        | 0                     | 1.89                | 0.655            |
| Octane    | Nonpolar     | Alkanes         | CH₃(CH₂)₉CH₃ | 114.2                     | 1.47                        | 0                     | 1.94                | 0.703            |
| Dibutylether | Ether  | Ether            | CH₃(CH₂)₉O | 130.2                     | 0.64                        | 0                     | 3.1                 | 0.769            |
| Mesitylene| Aromatic     | Aromatic        | C₆H₄(CH₃)₂  | 120.2                     | 0.23                        | 0                     | 2.4                 | 0.864            |

**Figure 2.** a) Optical images showing the patterns after complete solvent evaporation on the circular interdigitated microelectrodes. I) µ-rivulet deposition pattern obtained from a 0.5 µL droplet of AuNPs suspended in a 80/20 toluene/nonane solution. The surface tilt angle was ~30°. II) Spreading deposition pattern from a 0.5 µL droplet of AuNPs suspended in 100% toluene. The surface tilt angle was ~60°. b) I–III) AFM scans for the µ-rivulet deposition pattern along the droplet trail. I) The start, II) the intermediate, and III) the end regions of the deposited trail. IV) AFM scan for the spreading deposition pattern and V) Zoom-in on a smaller part of (IV).
concentration, whereas for others decreased monotonically, depending on the VOC type and humidity level (Section III, Figures S2 and S3, Supporting Information). In many cases, these sensors had superior analytical parameters (e.g., limit of detection, sensitivity, selectivity, etc.) than sensors based on other nanomaterials (CNT, graphene, metal oxide) and/or deposition techniques. The superiority of these newer sensors is demonstrated by recalling that they can detect VOCs down to ppb levels not only under arid conditions, but also in high humid atmospheres (≈90% RH), where most currently available sensors fail (ref. [1] and bibliography therein).

The heat maps in Figure 3 represent the relative resistance changes of the six sensors after exposure to the different VOC levels (100–1000 ppb) in arid conditions, intermediate humidity, and high humidity levels. The first three columns in the heat map belong to the µ-rivulet sensors and the other three belong to the SP sensors. The rows in each heat map represent the eight different VOCs to which the sensors were exposed. Comparing the sensing signals in Figure 3, some of the sensors showed an increase in their response at all three humidity levels when higher VOCs concentrations were introduced. On the other hand, other sensors gave lower responses under the same conditions. As a representative example, the response of the SP-C_{12} sensor to 100 ppb of decane at 0% RH (red squares in the first heat map) started to decrease with increasing decane concentration, as evidenced by the successive color shift from red to green and then to light blue (see the corresponding squares for decane measurements with the same SP-C_{12} sensor in the successive heat maps toward the right); the response decreases from ≈0.3% at 100 ppb to ≈0.05% at 1000 ppb of decane. The same sensor exposed to decane at 30% RH increased its response, as seen from the corresponding colors in Figure 3; the response increased from ≈0.7% at 100 ppb to ≈1% at 1000 ppb in this case. The increase or decrease in the responses of all sensors was in good approximation proportional (linear) to increasing VOC concentration. For the same aforementioned example, increase and decrease in response were proportional to a correlation coefficient of 0.97.

Further examination of Figure 3 shows that the sensors were more selective toward the different VOCs in the arid atmosphere than in the humidified backgrounds. The SP-C_{12} sensor was the most selective one in discriminating between the different kinds of VOCs. Scrutinizing Figure 3, the values of the

| Sensor type | Abbreviation |
|-------------|--------------|
| µ-Rivulet   | µR-C_{6}     |
| µ-Rivulet   | µR-C_{12}    |
| µ-Rivulet   | µR-C_{18}    |
| Spreading droplet | SP-C_{6} |
| Spreading droplet | SP-C_{12} |
| Spreading droplet | SP-C_{18} |

Table 2. The six sensors fabricated and examined in the present study.
relative resistance changes are higher with increasing humidity, ranging between 0.05% and 0.4% at 0% RH; between 0.2% and 2% at 30% RH; and between 0.5% and 3% at 90% RH. This could be related to the effect of the water molecules on charge transport into the chemiresistive film. Although higher humidity levels lowered the selectivity of the sensors, very good responses to the different VOCs were nevertheless obtained at these humidity levels.[17]

From the sensing response curves, the sensitivity of each sensor was calculated as the gradient of the relative response versus concentration (Section IV, Figure S4 in the Supporting Information). At 0% RH, the µ-rivulet sensor of AuNPs with the C₁₈ had the highest sensitivity compared with the other two ligands (Figure 4a,I). This Figure also indicates that the longer the ligand the more sensitive the sensor fabricated with the related deposition pattern. For example, on exposure to octanol, the sensitivities of the C₆, C₁₂, and C₁₈ ligands were 1.24 × 10⁻⁴, 2.07 × 10⁻⁴, and 2.21 × 10⁻⁴, respectively. The same trend was seen after exposure to all studied VOCs, except for mesitylene. In this case, the C₆ ligand was more sensitive than C₁₂ (3.21 × 10⁻⁵ and 7.28 × 10⁻⁶, respectively). For the SP sensors (Figure 4a,II) there was no preference for one ligand relatively to the others. C₁₂ was the most sensitive to octanol, decane and mesitylene, while C₁₈ was the most sensitive to ethanol, octane, and hexane.

In Figure 4b, the effect of the printed pattern on the sensitivity value for the three humidity levels is shown for three ligand types, C₆, C₁₂, and C₁₈. Figure 4b,I presents the data for C₆. The bars relating to the SP pattern are higher than the bars for the µ-rivulet pattern at all three RH levels and for all VOCs. For example, after exposure to octanol at 0% RH, SP pattern sensitivity was 2.73 × 10⁻⁴, whereas µ-rivulet pattern sensitivity was 1.24 × 10⁻⁴ (i.e., nearly twice higher); at 30% RH, SP pattern sensitivity was 1.91 × 10⁻⁴, whereas µ-rivulet pattern sensitivity was 5 × 10⁻⁵ (i.e., ~4 times higher); at 90% RH, SP sensitivity was 2.2 × 10⁻⁵, whereas µ-rivulet pattern sensitivity was 5 × 10⁻⁵ (i.e., ~4.4 times higher). This trend was not maintained for 1-dodecanethiol (C₁₂) (Figure 4b,II). In this latter case, SP pattern gave an even higher sensitivity in comparison with the µ-rivulet pattern on exposure to some VOCs such as octanol, hexanol, decane and mesitylene, whereas exposure of the µ-rivulet pattern to ethanol, octane, hexane and dibutylether gave greater sensitivities. Finally, an opposite trend occurred with the C₁₈. Figure 4b,III shows that µ-rivulet was more sensitive than SP after exposure to all VOCs at the three humidity levels. Differences in sensitivity using the three different ligands used could be attributed to differences in the morphology of the sensing layer (Section II, Supporting Information).
The discriminative capability of the investigated sensors array at different humidity levels was investigated by the statistical analysis of their collective responses, using a supervised linear multivariate data analysis method (discriminant factor analysis; DFA)—see the Experimental Section for more details. Figure 5a shows the DFA plots derived from the resistance responses of the sensors. These plots present the separation between all eight VOCs tested using the six sensors array; good discrimination between the VOCs can be observed at all RH levels, especially at 90% RH. The data points were not clustered at 0% RH but spread out toward the periphery. The directions of the arrows indicate increasing concentration of each VOC. As humidity increased, the data points became more clustered with less overlapping between them. The accuracy of this separation was calculated for each couple of VOCs tested using leave-one-out cross validation, as shown in the heat maps from Figure 5b. High accuracy values (80%–100%) were obtained in all binary separations, indicating high separation ability of the sensors array between every pair of VOCs tested. Once again, Figure 5b emphasizes the fact that the higher the humidity level, the higher the accuracy of discrimination.

We also investigated the ability of the sensors array to separate the group of polar from the group of nonpolar VOCs at the three humidity levels (Figure 6a). Good separation occurred at all three humidities. The classification accuracy between the polar and nonpolar VOCs was 79.2% at 0% RH, and increased to 87.5% at 30% RH and to 85.4% at 90% RH. This led to data points that were better separated and lowered the overlapping between them for the humidified backgrounds, i.e., improving the separation results (the classification results are summarized in Table 3). Focusing on the polar VOCs, Figure 6b shows that DFA analysis distinguishes between the three polar analytes at all three RH levels (i.e., octanol, hexanol, and ethanol). Again, as the humidity background increased, the separation improved as well as the classification accuracy (summarized in the Part A of Table 3). Similar analysis of the nonpolar group of VOCs (Figure 6c) gave the same trend, higher classification accuracy being obtained at 90% RH.

DFA analysis were also performed separately with the data of the SP droplet and μ-rivulet sensors. The separation accuracy of these two analyses is summarized in the Parts B and C of Table 3. Spreading sensors could differentiate between the different polar VOCs with a 94.4% accuracy at all three humidity levels, whereas the accuracy achieved with μ-rivulet sensors increased with increase in the humidity level, from 66.7% at 0% RH to 100% at 90% RH. The μ-rivulet sensors array was also superior in the discrimination of nonpolar VOCs at 0% RH.

To examine the suitability of the sensor arrays for integration into smart self-training sensors platform, models for predicting the real concentration of the VOCs were built using the partial least-square (PLS) method (see Experimental Section for more details). Table 4 presents the information regarding the correlation coefficient (CC) between the real and predicted concentrations for each VOC analyzed at the three RH levels. The more closely the CC values to unity, the better the estimation of the real concentration of the specific VOC.
Excellent prediction \((CC > 0.98)\) was obtained by the six sensors array for hexanol, decane and mesitylene at all three RHs, and for octanol at 0% RH. Part (b) of Table 4 and Figure 7 show the excellent prediction of the six sensors array for octanol concentrations at 0% RH, given as an illustrative example; the high sensitivity of the sensors array is proven by accurately predicting values as low as 100 ppb for octanol. Very high CC values were obtained for all VOCs at 0% RH, indicating that excellent estimation of their concentrations can be obtained after exposing the sensors array to unknown VOCs concentrations. High CC values also were obtained for almost all VOCs at high humidity levels, meaning that this sensors array still performs well in humidified conditions.

Figure 6. a) DFA results showing the discrimination between the groups of polar and nonpolar VOCs at 100, 200, 400, 600, 800, and 1000 ppb, at I) 0% RH, II) 30% RH, and III) 90% RH, using the array of six sensors. b) DFA discrimination results between the polar VOCs achieved with the six sensors array at the three humidity levels (I)–(III). c) Similar DFA discrimination for the nonpolar VOCs.

Table 3. Classification accuracy achieved through leave-one-out cross validation by (A) the entire sensors array, (B) the three sensors based on spreading deposition pattern, and (C) the three sensors based on \(\mu\)-rivulet deposition pattern.

| DFA model                                      | Classification accuracy |
|-----------------------------------------------|-------------------------|
|                                               | 0% RH  | 30% RH | 90% RH | All data (at all RH levels) |
| A. Entire six sensors array                   | 79.2%  | 87.5%  | 85.4%  | 75.7%                      |
| Polar versus nonpolar VOCs                    | 94.4%  | 100%   | 100%   | 92.6%                      |
| Differentiating between polar VOCs            | 83.3%  | 83.3%  | 90.0%  | 71.1%                      |
| Differentiating between nonpolar VOCs         |        |        |        |                            |
| B. Sensors based on spreading deposition pattern| 72.9%  | 75.0%  | 64.6%  | 60.4%                      |
| Polar versus nonpolar VOCs                    | 94.4%  | 94.4%  | 94.4%  | 87.0%                      |
| Differentiating between polar VOCs            | 66.7%  | 66.7%  | 80.0%  | 56.7%                      |
| Differentiating between nonpolar VOCs         |        |        |        |                            |
| C. Sensors based on \(\mu\)-rivulet deposition pattern | 70.8%  | 83.3%  | 79.2%  | 68.8%                      |
| Polar versus nonpolar VOCs                    | 66.7%  | 77.8%  | 100.0% | 81.5%                      |
| Differentiating between polar VOCs            | 73.3%  | 60.0%  | 80.0%  | 57.8%                      |

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When considering the concentration prediction performances of the SP and µR sensor arrays separately, the former sustains the same high quantification capability, whereas the µR sensors array is generally less accurate in performing the quantification task (parts (c) and (d) of Table 4).

### 3. Summary and Conclusions

We described the fabrication of ultrasensitive cross-reactive sensor arrays by a new printing technique that relies on a single droplet of AuNPs. Two different line patterns were printed over...
interdigitated microelectrodes, and their sensing performance towards various VOCs was compared. The sensors showed ultrasensitivity toward very low concentrations of different types of VOCs at very low concentrations in the range from 100 to 1000 ppb. Differences in sensitivity were obtained between the two printed patterns by the AuNPs capped by ligands of different lengths (C₆, C₁₂, and C₁₈). We conclude that the µ-rivulet pattern deposition of AuNPs capped with the longest ligand is more sensitive than with shorter ligand lengths. On the other hand, the spreading pattern proved more sensitivity than the µ-rivulet pattern for shorter ligands, whereas with the longer ligands the result was opposite. The effect of humidity showed that the printed sensor arrays behaved well even under extremely humid ambient conditions (90% RH), suggesting successful production of highly robust sensors that can serve for a wide range of real-world sensing applications. The printed cross-reactive sensors array also possesses a reliable and excellent ability to discriminate between different types of VOCs. Employing the PLS algorithm, we showed that this sensors array could predict VOCs concentrations with high accuracy at different humidity levels, which can be of greatest interest in the construction of smart self-learning sensing systems. Our novel approach open the door to a new generation of sensors and allow full control over sensing layer morphology. Enhancements through integration with high resolution dispensing systems and accurate droplet actuation techniques should create greater fabrication opportunities for a wider range of 0D, 1D, and 2D nanomaterials.

4. Experimental Section

Synthesis of Monolayer-Capped Gold Nanoparticle Solutions: Three sets of monolayer-capped gold nanoparticles (AuNPs), capped with 1-hexanethiol (C₆), 1-dodecanethiol (C₁₂), and 1-octadecanethiol (C₁₈) were synthesized using the Brust method. Unless otherwise indicated, all materials used in the synthesis process came from Sigma-Aldrich, Israel. Synthesis briefly involves a solution of HAuCl₄ being added to a stirred solution of tetracetyl ammonium bromide (TOAB) in toluene. After stirring for 10 min, the lower aqueous phase was removed. Organic alkanethiol ligands and sodium borohydride were added to the toluene phase. After 3 h at 1–4 °C, the lower aqueous phase was removed, and the toluene phase was removed by rotary evaporation. After first washing with cold dry ethanol, the solution was kept at 5 °C for 18 h until the dark brown material fully precipitated, which was filtered off and washed with ethanol. This procedure was repeated three times to remove all residual ions, such as TOAB. The nanoparticles were resuspended into toluene to get concentrated solutions of gold nanoparticles. The final solutions from which the sensors were prepared were diluted in toluene to 60 mg mL⁻¹, or in a mixture of toluene and nonane (80%/20% by volume).

Sensors Fabrication: Droplets of AuNPs were actuated over a Si wafer of 600 µm thickness with a 0.6 µm thermal oxide layer and 3000 µm circular interdigitated Au electrodes patterned on top. The substrates were cleaned before use by rinsing in acetone, ethanol, and isopropylalcohol, followed by drying with nitrogen. They were exposed to UV light and ozone with a Novascan PSD Pro UV Ozone system. Note: The effect of hydrophobic or hydrophilic nature of the substrate’s surface had a negligible effect on the quality of the actuation of the AuNPs’ droplet. To reach the desired deposition pattern, the substrates were inclined on an adjustable angling device. After deposition, the devices were dried in a vacuum oven at 50 °C for 2 days.

Characterization: AuNPs shape and size were characterized by transmission electron microscopy (TEM). Their deposition patterns were characterized by AFM imaging, using a NanoWizard III NanoScience AFM instrument with Top View Optics (IPK Instruments AG, Germany). Small-scale distance measurements of the different pattern features (e.g., µ-rivulet ridge widths, w) were measured using a Nikon Eclipse LV150N optical microscope with a ×150 bright-field objective.

Exposure to VOCs: The sensors were exposed to a series of VOCs at 100, 200, 400, 600, 800, and 1000 ppb, using a gas generator system. A Keithley data logger device (model 2701 DMM) controlled by a custom Labview program was used to sequentially acquire resistance readings from the sensors. A typical exposure cycle carried out inside a 330 cm³ stainless-steel chamber involved a 5 min vacuum (≤50 mTorr) baseline step, followed by a 5 min exposure to the VOCs, and ended with another 5 min vacuum step. The process was repeated twice for each VOC at each concentration. The gaseous mixtures were produced using a commercial permeation/diffusion tube dilution (PDTD) system (Umwelttechnik MCZ, Germany). Purified dry nitrogen (99,99999%) from a commercial nitrogen generator (N-30, On Site Gas Systems, USA) equipped with a nitrogen purifier was used as the carrier gas. The PDTD system used a temperature controlled oven to mix a constant flow (200 ± 1 cm³ min⁻¹) of purified nitrogen with a constant mass flow of a vaporized VOC exiting a diffusion tube (Dynacal, VICI Metronics). The mixture exiting the system was diluted again with nitrogen to the desired concentrations. VOC concentration was determined by controlling the mass flow rate of the vaporized VOC (through temperature control of the diffusion tubes) and the total volumetric nitrogen flow rate. The concentrations were verified using a commercial photoionization detector (VOC-TRAQ, Bronze pID-TECH plus, Baseline-Mocoon Inc., USA). Controlled relative humidity levels (0%–90% RH) were obtained by mixing dry nitrogen with humidified air generated by the system’s humidifier module.

Data Analysis: Data classification involved a DFA algorithm. DFA is a supervised linear method supplied with the classification information regarding every measurement in the training set. It finds new orthogonal axes (canonical variables) as a linear combination of the input variables, computing these factors to minimize the variance within each class and maximize the variance between classes. Prediction accuracy was calculated using the leave-one-out cross-validation method. Given n measurements, the pattern recognition model was computed n times using n−1 training vectors. The vector left out during the training phase (i.e., the validation vector, hidden by the algorithm during the training

4. Experimental Section

Synthesis of Monolayer-Capped Gold Nanoparticle Solutions: Three sets of monolayer-capped gold nanoparticles (AuNPs), capped with 1-hexanethiol (C₆), 1-dodecanethiol (C₁₂), and 1-octadecanethiol (C₁₈) were synthesized using the Brust method. Unless otherwise indicated, all materials used in the synthesis process came from Sigma-Aldrich, Israel. Synthesis briefly involves a solution of HAuCl₄ being added to a stirred solution of tetracetyl ammonium bromide (TOAB) in toluene. After stirring for 10 min, the lower aqueous phase was removed. Organic alkanethiol ligands and sodium borohydride were added to the toluene phase. After 3 h at 1–4 °C, the lower aqueous phase was removed, and the toluene phase was removed by rotary evaporation. After first washing with cold dry ethanol, the solution was kept at 5 °C for 18 h until the dark brown material fully precipitated, which was filtered off and washed with ethanol. This procedure was repeated three times to remove all residual ions, such as TOAB. The nanoparticles were resuspended into toluene to get concentrated solutions of gold nanoparticles. The final solutions from which the sensors were prepared were diluted in toluene to 60 mg mL⁻¹, or in a mixture of toluene and nonane (80%/20% by volume).

Sensors Fabrication: Droplets of AuNPs were actuated over a Si wafer of 600 µm thickness with a 0.6 µm thermal oxide layer and 3000 µm circular interdigitated Au electrodes patterned on top. The substrates were cleaned before use by rinsing in acetone, ethanol, and isopropylalcohol, followed by drying with nitrogen. They were exposed to UV light and ozone with a Novascan PSD Pro UV Ozone system. Note: The effect of hydrophobic or hydrophilic nature of the substrate’s surface had a negligible effect on the quality of the actuation of the AuNPs’ droplet. To reach the desired deposition pattern, the substrates were inclined on an adjustable angling device. After deposition, the devices were dried in a vacuum oven at 50 °C for 2 days.

Characterization: AuNPs shape and size were characterized by transmission electron microscopy (TEM). Their deposition patterns were characterized by AFM imaging, using a NanoWizard III NanoScience AFM instrument with Top View Optics (IPK Instruments AG, Germany). Small-scale distance measurements of the different pattern features (e.g., µ-rivulet ridge widths, w) were measured using a Nikon Eclipse LV150N optical microscope with a ×150 bright-field objective.

Exposure to VOCs: The sensors were exposed to a series of VOCs at 100, 200, 400, 600, 800, and 1000 ppb, using a gas generator system. A Keithley data logger device (model 2701 DMM) controlled by a custom Labview program was used to sequentially acquire resistance readings from the sensors. A typical exposure cycle carried out inside a 330 cm³ stainless-steel chamber involved a 5 min vacuum (≤50 mTorr) baseline step, followed by a 5 min exposure to the VOCs, and ended with another 5 min vacuum step. The process was repeated twice for each VOC at each concentration. The gaseous mixtures were produced using a commercial permeation/diffusion tube dilution (PDTD) system (Umwelttechnik MCZ, Germany). Purified dry nitrogen (99,99999%) from a commercial nitrogen generator (N-30, On Site Gas Systems, USA) equipped with a nitrogen purifier was used as the carrier gas. The PDTD system used a temperature controlled oven to mix a constant flow (200 ± 1 cm³ min⁻¹) of purified nitrogen with a constant mass flow of a vaporized VOC exiting a diffusion tube (Dynacal, VICI Metronics). The mixture exiting the system was diluted again with nitrogen to the desired concentrations. VOC concentration was determined by controlling the mass flow rate of the vaporized VOC (through temperature control of the diffusion tubes) and the total volumetric nitrogen flow rate. The concentrations were verified using a commercial photoionization detector (VOC-TRAQ, Bronze pID-TECH plus, Baseline-Mocoon Inc., USA). Controlled relative humidity levels (0%–90% RH) were obtained by mixing dry nitrogen with humidified air generated by the system’s humidifier module.

Data Analysis: Data classification involved a DFA algorithm. DFA is a supervised linear method supplied with the classification information regarding every measurement in the training set. It finds new orthogonal axes (canonical variables) as a linear combination of the input variables, computing these factors to minimize the variance within each class and maximize the variance between classes. Prediction accuracy was calculated using the leave-one-out cross-validation method. Given n measurements, the pattern recognition model was computed n times using n−1 training vectors. The vector left out during the training phase (i.e., the validation vector, hidden by the algorithm during the training
phase, and completely new for the training model) was then projected onto the model built, producing a classification result. All possibilities of the leave-one-sample-out were considered, and the classification accuracy was estimated as the averaged performance over n tests. A linear multivariate statistical algorithm, specifically PLS, was used to build predictive models for estimating VOCs concentrations. PLS is a multivariate calibration method that attempts to find factors (i.e., latent variables) that capture as much variance as possible in the predictor block (responses matrix) under the constraint of being correlated with the predicted block (concentrations matrix). The prediction of VOCs concentration was estimated using a leave-one-out cross-validation method. Thus, for each VOC, a model was built n times using n – 1 measurements, and the remaining one was used for testing.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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