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Preliminary Analysis on a Paper-based Ammonia Sensor for Future Food Smart Packaging

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Abstract— Here, we report a preliminary analysis on the manufacturing and testing of a low-cost and eco-friendly paper-based gas sensors realized with Aerosol Jet Printing (AJP) and Flash Lamp Annealing (FLA). The hygroscopic properties of paper make it possible to detect the presence of water-soluble gases in an environment provided with a relative humidity (RH) above a given threshold ($RH > 75\%$). This aspect allows the usage of such technology in the realization of a future food smart packaging detecting the presence of a malevolent gas like ammonia in food. Carbon interdigitated electrodes were printed and sintered on chromatographic paper, obtaining a mean resistance value of $(231 \pm 20) \text{ k}\Omega$ and $(249 \pm 28) \text{ k}\Omega$ for the left and the right electrode respectively. The sensors were tested at different relative humidity (RH) values (75, 80, 90, 100%), and once stabilized they were tested with different ammonia concentrations (3, 6, 9 and 12 ppm). A proportional decrease was evidenced in increasing RH and ammonia concentration. Considering the baseline at a constant value of $RH=75\%$, the sensors showed a resistance decrease of 15% in presence of the lowest concentration of 3 ppm.

Keywords—aerosol jet printing, flash lamp annealing, paper-based sensors, gas sensors, ammonia, smart object, smart packaging

I. INTRODUCTION

Food loss and waste is one of the greatest challenges of this century, since it is a promoter of economic and social consequences and generating environmental changes like freshwater depletion, biodiversity loss, ecosystems pollution [1]. New efforts and technological advances must be made to prevent food waste and its correlated phenomena from becoming more and more severe. In such a kind of context, a significant advancement could be represented by food smart packaging. New packaging systems can be designed with embedded measuring devices to monitor changes in the product communicating the acquired information to operators and/or consumers, thus increasing products' traceability and safety [2].

Ammonia and its compounds are one of the most troubleshooting pollutants due to their toxicity to human body being responsible of severe pathologies (from migraine and allergies to carcinogenesis) [3]–[5]. Examples of sensors for monitoring the presence of these compounds in different environments could be air pollution sensors working at near-room temperature [6] or humidity-ammonia sensors for aviculture centers, using conductive polymers [7]–[9] or hybrid solutions [3], [4].

Ammonia presence should also be strictly monitored in foods to confirm a ceased edibility, since it is also connected to meat degradation, [5]. A first example of food smart packaging for ammonia detection has been developed using a hybrid structure made of printed sensors and a silicon chip. However, this device presented some delicate aspects regarding the device-packaging bond that may be dependent on the operator and regarding employed glues that may in the long run invalidate the intended measurement [10]. In light of this, the possibility to directly print sensors on the package together with transponders could play a pivotal role in the production of a new kind of smart packaging with embedded measuring sensors.

Some printed electronics (PE) technologies can come to our rescue being able to print on any kind of surfaces, both rigid and flexible, planar and 3D showing flexibility together with reduced production cost, variety of materials to be used, capability to miniaturize sensors and circuits [11], [12]. In this wide family, Aerosol Jet Printing (AJP) presents several interesting characteristics like maskless and contactless direct printing on planar and 3D surfaces, low wastage of material, high customizability of printed patterns. The printing process sees the aerodynamic focusing of liquid particles, present in a container, and allows to manufacture printed features in the range of 10-3000 μm in width with tens of micrometers as maximum thickness. AJP is also characterized by a wide range of printable inks like biological materials, metals, insulators, semiconductors and also piezoelectric inks [13]–[15]. In order to reach their final properties, PE inks must be sintered/cured and considering typical food packaging materials, Flash Lamp Annealing (FLA) fits very well with such substrate materials. In this process, a couple of xenon flash lamps irradiate a light pulse absorbed by the printed features. The great advantage of this technology is to perform fast thermal treatments (millisecond scale) of printed thin films realized on low-melting point substrates (plastics, fabrics, paper-based materials, etc.) without damage and unwanted effects [16].

The combination of the above-mentioned technologies opens the way to a real smart packaging, which will be characterized by embedded sensors and communication elements able to exchange collected information about food with a dedicated external read-out unit in supermarkets, stores or in a food supply chain facility.

The aim of this work is to present a paper-based ammonia gas sensor entirely realized through AJP and FLA as first step in the realization of a passive wireless ammonia gas sensor for food smart packaging. The working mechanism of our sensor

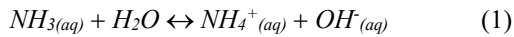
relies on the intrinsic hygroscopic characteristics of cellulose paper. Fibers inside paper contains moisture as a consequence of absorption from the surrounding environment, which promotes the electrical detection of water-soluble gases like ammonia. Electrical impedance or conductance variation of paper due to food degradation can be measured thanks to carbon electrodes realized on the surface of the paper sheet [17], [18]. Section II will present materials and methods followed in the manufacturing steps and during testing. Section III will show the experimental setup employed during the tests. Section IV will present and discuss the preliminary experimental results.

II. MATERIALS AND METHODS

In this section, sensors manufacturing process is explained considering materials involved and sensors layout (Section II-A and B), together with the manufacturing process (Section II-C), geometrical and electrical evaluation will be considered in Section II-D.

A. Physical measuring principle

Cellulose fibers present a certain amount of moisture, even if paper looks and feels dry, absorbed by the surrounding environment. Ammonia is a water-soluble gas, so when this element is placed inside a humidity saturated atmosphere the chemical reaction showed in (1) takes places.



Once kept fixed relative humidity and temperature, water quantity adsorbed is constant, and in light of this any impedance change is due to ammonia presence in a specific amount in the surrounding environment. Considering (1), an elevated ionic conductivity is generated by ammonium (NH_4^+) and hydroxide (OH^-) ions from the dissociation of ammonia in water, thus changing the impedance of paper which can be measured thanks to printed electrodes on paper surface.

B. Materials

WhatmanTM chromatography 1 cellulose paper was the selected substrate to avoid influences related to chemical additives, thanks to its higher degree of purity than that of commercial papers. Chromatographic paper is characterized by high hygroscopic properties, so that cellulose fibers contain a substantial amount of moisture. For example, at a relative humidity of 50%, paper contains ~5% water by weight. In case of dissociation of water-soluble gases on the surface of paper, ionic conductance increases due to additional ions presence.

A carbon ink (EXP 2652-28) was purchased by Creative Materials Inc. to realize the electrodes through which measure conductance changes. The ink (starting viscosity of 15-20 mPa·s) was properly atomized together with its own thinner during printing process to obtain a better printability and adhesion to the substrate.

C. Sensors design

AutoCAD was the software used for electrodes design. An interdigitated layout with two comb electrodes was selected to capture water soluble ions which lie between two consecutive fingers. As can be seen in Fig. 1, each comb electrode consists of 8 fingers with length 12 mm, and it was designed with finger width of 300 μ m, and a gap between two consecutive

fingers of 500 μ m. These quotes are respectively reported in Fig. 1 as l, w, and g.

D. Manufacturing process

Figure 2 presents the block diagram of the manufacturing process. An AJ300 model (Optomec, Albuquerque, NM, USA) was the aerosol jet printer machine involved in this work. Carbon interdigitated electrodes were printed designing a specific toolpath consisting in two consecutive overlapped depositions per run. Printing process parameters applied during the printing cycle are listed in Table and they were tuned in order to obtain the described geometrical performances. Process flows are expressed in standard centimeter cube per minute (SCCM). A total number of fifty sensors was manufactured, in five batches of ten sensors each one.

Right after printing step, Pulseforge 1300 (Novacentrix, Austin, TX, USA) was used to anneal the printed electrodes. Considering the previous study performed on finding the best sinter parameters, a single pulse was applied at a voltage of 250 V with a duration of 1750 μ s [17]. The printed layout is visible in Fig. 1, together with a magnification of the fingers.

E. Geometrical and electrical evaluation

The carbon interdigitated electrodes of the manufactured sensors were tested after printing in terms of geometrical stability and electrical properties. Resistance measurements were performed by means of the digital bench-top multimeter Hewlett-Packard 34401a considering the longest geometrical element. Considering the interdigitated layout, mean resistance values for left and right electrodes were respectively equal to (231 ± 20) k Ω and (249 ± 28) k Ω . Multimeter probes during measurements were placed in A-A points, as displayed in Fig. 1. The geometrical analysis was then performed on cellulose samples owing to an optical microscope by Orma Scientific NB50T (trinocular zoom 0.8x–5x–LED), with its devoted HDMI MDH5 camera model, was used to acquire the images (Orma Scientific, Sesto San Giovanni, Milan, Italy). Optical measurements confirmed what designed before printing: mean value of tracks' widths and gaps was respectively of 340 ± 0.05 μ m and 460 ± 0.03 μ m (relative standard deviation respectively of 13% and 8%), as can be seen in Fig. 1.

III. EXPERIMENTAL SETUP

Fig. 3 presents the scheme of the experimental setup used during our tests. A pneumatic circuit, composed by four mass flow controllers with relative tubing and wires, and a couple of vials, was placed inside a thermostatic chamber to keep fixed the temperature during tests (25 ± 2 °C). The circuit has been developed to manage the simultaneous presence of three gaseous components: dry air, humidity saturated air, and ammonia as basic analyte gas (Gas 1 in Fig. 3). Four mass flow controllers were employed to tune and control the fluxes during tests. MF-1 model (Andover, Massachusetts, USA) were the selected devices for our experiments, withstanding a maximum flow of 200 SCCM. We decided to work with a constant flux of 100 SCCM, the half of the maximum that can be delivered by our experimental setup. Considering Figure 3, the three of them placed at the left can be considered as mass flow controllers, the last one at the right can be considered as a mass flow meter to state the correct status of them system under working conditions.

Mass flow controllers were connected to an ISO-TECH power supplier (DC voltage set to 24 V) and via USB communication to a personal computer. Here, a devoted LabVIEW software was developed in order to properly mix the flow from certified bottles (SOL SpA, Italy) and thus control the atmospheric composition inside the test chamber. The saturated humidity line consisted of a vial partially filled with water, which served as bubbler. A resistive humidity sensor (Model IH-3610-1, Honeywell Inc., 24B Concord Street, El Paso, TX, USA) was placed inside testing chamber together with paper sensors as a feedback of the humidity level generated thanks to our bubbler. The circuit was designed in order to force the flux being pumped inside the second vial, which worked as the test chamber, where four sensors were simultaneously placed during tests. Each sensor was directly connected to a multimeter, data were sent thanks to a GPIB cable to a personal computer and acquired through a devoted LabVIEW software.

TABLE I. CARBON INK PROCESS PARAMETERS

Parameter	Printed material EXP 2652-28
Sheath gas flow (SCCM)	650
Atomizer gas flow (SCCM)	1140
Exhaust gas flow (SCCM)	1075
Plate Temperature (°C)	50
Printing speed (mm/s)	4
Runs number	3

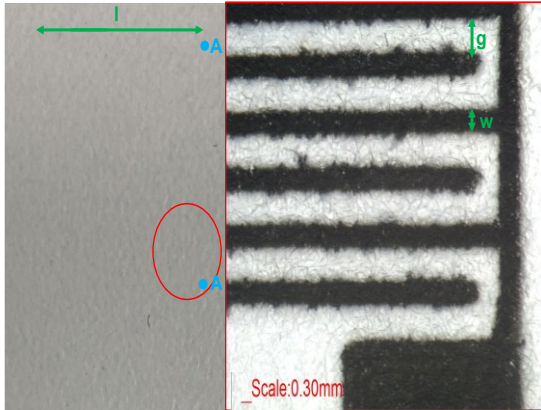


Fig.1. Sensors final layout on chromatographic paper and optical microscope magnification. $l=12$ mm, $g=500$ μ m, $w=300$ μ m. A-A points indicate where multimeter probes were placed of resistance measurements.

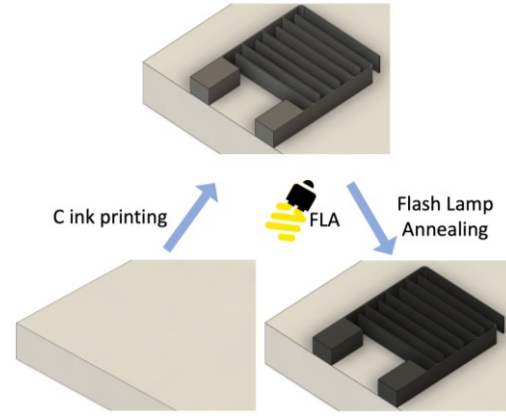


Fig. 2. Block diagram of the manufacturing process.

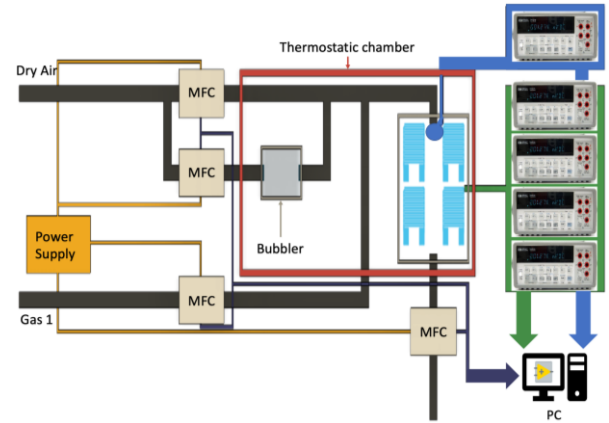


Fig. 3. Schematic representation of the experimental setup. The colors orange, black, red, violet and green indicate respectively the power supply to mass flow controllers, the gas flow tubings, the fixed temperature in the thermostatic chamber, mass flow controlling LabVIEW software, GPIB acquisition LabVIEW software. MFC indicates the mass flow controllers.

IV. PRELIMINARY RESULTS

The first part of the analysis was related to study the behavior of the sensors as a function of the humidity level, with no additional gases. In case of placing the sensors inside food packaging, the background will feature high relative humidity (RH) values. In a laboratory case study, we need to state the stabilization of the sensors at a different value of RH. This is necessary for the second part of the tests in which we introduced ammonia. In light of this, we considered as possible RH values 75%, 80%, 90% and 100%. The reason why we did not consider a lower RH is that they would be too far from RH food-packaging typical values and because at such levels their behavior would become too much resistive.

In Table II the obtained results were listed. RH=75% was the first conditioning step considered. Humidity was then increased after stabilization was reached at each value. In this stage of the tests, we noticed that a period of 8 h can be defined as sufficient to reach stabilization for RH=75 and 80%, while for RH=90% and 100% the mandatory time interval for a complete stabilization decreases to 3 h. Once stabilized in the humidity saturated environment, the same sensors were exposed to the same set of humidity values as before but in decreasing order. As can be seen in Fig. 4, RH=75% showed a stabilized mean resistance value lower about two orders of magnitude, if reached after stabilization at higher values of humidity. In this working condition, the

minimum necessary time interval to stabilize the sensors were respectively 3 h at RH= 90% and 4 h at RH=80, 75%.

The humidity test was repeated a second time was performed in order to evidence a possible hysteresis; Fig. 4 highlighted that no significant hysteresis happened, with an offset that reaches a peak of 11% at only RH=80%.

This result stated that our sensors desorbed moisture in a long period of time. In light of this, these sensors can work in a stable way at lower value of RH after being placed in a totally humidity saturated environment. In view of these results, the first treatment at high humidity level (blue curve in Fig. 4) emerges as a suitable pre-treatment to achieve stable (with no hysteresis) properties.

The second part of the tests was focused on the study the behavior of these paper-based sensors, inside a moist environment, with different concentrations of ammonia. A cyclic test was performed in order to evaluate possible hysteresis feeding ammonia. We started reaching a stable working condition after two consecutive stabilizations at RH=100% and 75%. Then ammonia was pumped inside the testing chamber with a concentration about 3 ppm. This amount was step by step increased by the same amount of 3 ppm after reaching stable resistance values, until a maximum concentration of 12 ppm was reached. Each ammonia concentration was kept fixed for a period of 4 h; after the peak values of 12 ppm, previous concentrations were restored in the same order (12, 9, 6, 3 ppm). A new air flux, without ammonia gas, with RH=75% was restored at the end of this second cycle.

Fig. 5 presented the mean resistance values obtained for each sensor, from 0 ppm (only air flux at RH=75%) to 12 ppm of ammonia. Each plotted point is an average value calculated over the stable portion of each period of feeding of each ammonia concentration, i.e., approximately the last 2 hours of the total 4-hour interval. A mean relative standard deviation of 2% was found.

It can be noted that a strong decrease is present in the interval 0-3 ppm, evidencing the capability of such sensors to trace ammonia presence inside the working environment. Furthermore, each increase of ammonia concentration matched with a proportional decrease of resistance in the range 2-4% compared to the previous resistance value. This fact is clearer in Fig. 6, where data are shown in terms of relative variation. ΔR represented the difference between the average resistance of the sensors used at RH=75%, 0 ppm once stabilized (R_0) and the mean resistance of the employed sensors at a specific ammonia concentration. Once again, it is visible the decrease in resistance proportional to each concentration considered. A second aspect is related to hysteresis cycle performed visible in Fig. 6, evidencing that no significant variation took place.

TABLE II. STABILIZATION AT DIFFERENT RH VALUES.

RH (%)	Measured quantities		
	Testing time (h)	Mean Resistance (M Ω)	Relative Standard Deviation (%)
75	24	102.6	7
80	12	46.2	10
90	12	5.9	8
100	10	3.8	2
90	14	4.3	4
80	24	5.2	5
75	29	6.4	5
75	8	5.9	5
80	8	4.7	3
90	4	4.2	2
100	4	3.6	2

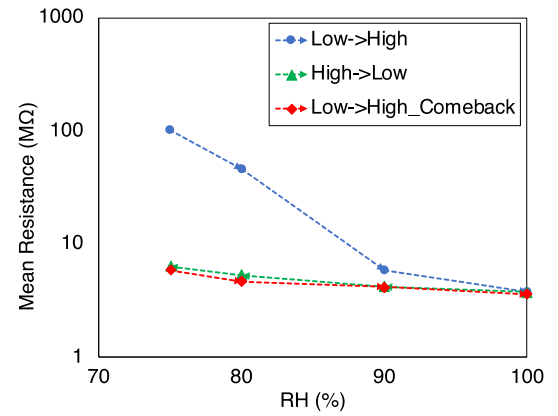


Fig. 4. Stabilization and hysteresis cycle of the sensors at different relative humidity. Blue curve represents the first study, from RH=75% to RH=100%; the green one the comeback to lower RH values, the red one the comeback to higher RH values.

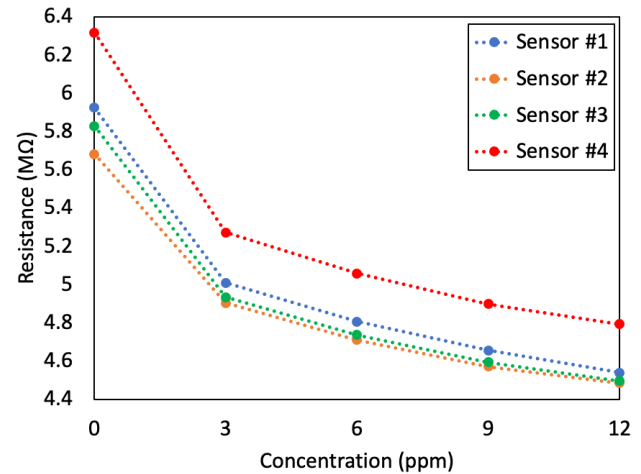


Fig. 5. Resistance values for each sensor at different ammonia concentrations, from 0 ppm to 12 ppm.

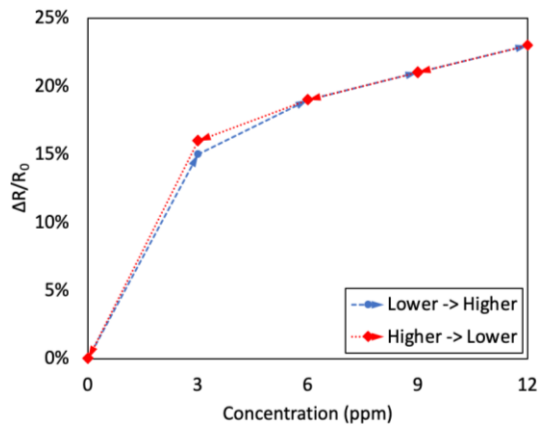


Fig. 6. Average percent increases for sensors tested at different ammonia concentrations. Hysteresis cycle tested: blue curve = starting cycle from 0 ppm to 12 ppm, red curve = come back cycle from 12 ppm to 0 ppm.

V. CONCLUSIONS

A paper-based gas sensor was proposed by means of Aerosol Jet Printing and Flash Lamp Annealing. The combination of such technologies showed good reproducibility despite a porous and extremely cheap sensing material such as chromatographic paper. Thanks to hygroscopic properties of paper, these sensors were tested against the presence of a water-soluble gas like ammonia, commonly present in degradation food processes. The sensors were firstly tested in a damp environment, considering different RH values from 75% to 100%. The sensors have shown to reach a stability after several hours depending on the humidity considered. In order to keep close to the conditions of the food environment, it was chosen to first set a condition of total saturation (3.8 MΩ, relative standard deviation 2%), then modified to a RH=75% kept constant (6.4 MΩ, relative standard deviation 5%). After this first step, ammonia was introduced in the test in different concentrations ranging from 0 ppm to 12 ppm in step of 3 ppm. The results evidenced the capability of the sensors to correctly detect the presence of ammonia starting from the lowest concentration showing a resistance decrease of 15% respect to the humidity background. The results in presence of ammonia confirmed no significant hysteresis phenomenon since no significant variation occurred during a cycle of rising and falling ammonia concentrations. Future developments will consider crosstalk analysis aiming to state the selectivity of these paper-based sensors in detecting ammonia in presence of possible interferent gases. Also tests at lower temperatures, proximal to food industry cold chain will be considered to study the influence of environmental temperature to sensing capabilities of these devices. A last step will regard printing tests directly on food packaging and a possible communicating wireless system dedicated to this kind of sensors.

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REFERENCES

- [1] M. Springmann *et al.*, "Options for keeping the food system within environmental limits," *Nature*, vol. 562, no. 7728, pp. 519–525, Oct. 2018.
- [2] S. Chen, S. Brahma, J. Mackay, C. Cao, and B. Aliakbarian, "The role of smart packaging system in food supply chain," *J. Food Sci.*, vol. 85, no. 3, pp. 517–525, Mar. 2020.
- [3] R. Ghosh, A. K. Nayak, S. Santra, D. Pradhan, and P. K. Guha, "Enhanced ammonia sensing at room temperature with reduced graphene oxide/tin oxide hybrid films," *RSC Adv.*, vol. 5, no. 62, pp. 50165–50173, Jun. 2015.
- [4] A. Maity, A. K. Raychaudhuri, and B. Ghosh, "High sensitivity NH₃ gas sensor with electrical readout made on paper with perovskite halide as sensor material," *Sci. Rep.*, vol. 9, no. 1, pp. 1–10, Dec. 2019.
- [5] C. Douny *et al.*, "Development of an Analytical Method for the Simultaneous Measurement of 10 Biogenic Amines in Meat: Application to Beninese Grilled Pork Samples," *Food Anal. Methods*, vol. 12, no. 10, pp. 2392–2400, Oct. 2019.
- [6] R. Ghosh, J. W. Gardner, and P. K. Guha, "Air Pollution Monitoring Using Near Room Temperature Resistive Gas Sensors: A Review," *IEEE Trans. Electron Devices*, vol. 66, no. 8, pp. 3254–3264, Aug. 2019.
- [7] R. M. Morais, M. D. S. Klem, G. L. Nogueira, T. C. Gomes, and N. Alves, "Low Cost Humidity Sensor Based on PANI/PEDOT:PSS Printed on Paper," *IEEE Sens. J.*, vol. 18, no. 7, pp. 2647–2651, Apr. 2018.
- [8] A. H. Ismail, N. A. Mohd Yahya, M. H. Yaacob, M. A. Mahdi, and Y. Sulaiman, "Optical ammonia gas sensor of poly(3,4-polyethylenedioxythiophene), polyaniline and polypyrrole: A comparative study," *Synth. Met.*, vol. 260, p. 116294, Feb. 2020.
- [9] A. Pasha, S. Khasim, F. A. Khan, and N. Dhananjaya, "Fabrication of gas sensor device using poly (3, 4-ethylenedioxythiophene)-poly (styrenesulfonate)-doped reduced graphene oxide organic thin films for detection of ammonia gas at room temperature," *Iran. Polym. J. (English Ed.)*, vol. 28, no. 3, pp. 183–192, Mar. 2019.
- [10] H. Zhou, S. Li, S. Chen, Q. Zhang, W. Liu, and X. Guo, "Enabling Low Cost Flexible Smart Packaging System with Internet-of-Things Connectivity via Flexible Hybrid Integration of Silicon RFID Chip and Printed Polymer Sensors," *IEEE Sens. J.*, vol. 20, no. 9, pp. 5004–5011, May 2020.
- [11] Y. Gu, D. Park, S. Gonya, J. Jendrisak, S. Das, and D. R. Hines, "Direct-write printed broadband inductors," *Addit. Manuf.*, vol. 30, p. 100843, Dec. 2019.
- [12] A. S. Almuslem, S. F. Shaikh, and M. M. Hussain, "Flexible and Stretchable Electronics for Harsh-Environmental Applications," *Adv. Mater. Technol.*, vol. 4, no. 9, p. 1900145, Sep. 2019.
- [13] B. Clifford, D. Beynon, C. Phillips, and D. Deganello, "Printed-Sensor-on-Chip devices – Aerosol jet deposition of thin film relative humidity sensors onto packaged integrated circuits," *Sensors Actuators, B Chem.*, vol. 255, pp. 1031–1038, Feb. 2018.
- [14] N. J. Wilkinson, M. A. A. Smith, R. W. Kay, and R. A. Harris, "A review of aerosol jet printing—a non-traditional hybrid process for micro-manufacturing," *Int. J. Adv. Manuf. Technol.*, 2019.
- [15] J. Ouyang, D. Cormier, S. A. Williams, and D. A. Borkholder, "Photonic Sintering of Aerosol Jet Printed Lead Zirconate Titanate (PZT) Thick Films," *J. Am. Ceram. Soc.*, vol. 99, no. 8, pp. 2569–2577, 2016.
- [16] S. Das, D. Cormier, and S. Williams, "Potential for Multi-functional Additive Manufacturing Using Pulsed Photonic Sintering," in *Procedia Manufacturing*, 2015, vol. 1, pp. 366–377.
- [17] E. Cantù, M. Soprani, A. Ponzoni, E. Sardini, and M. Serpelloni, "Preliminary Analysis on Cellulose-based Gas Sensor by Means of Aerosol Jet Printing and Photonic Sintering," 2020.
- [18] G. Barandun *et al.*, "Cellulose Fibers Enable Near-Zero-Cost Electrical Sensing of Water-Soluble Gases," *ACS Sensors*, vol. 4, no. 6, pp. 1662–1669, Jun. 2019.