

Inkjet-printed, flexible, high performance, carbon nanomaterial based sensors for ammonia and DMMP gas detection

Jimmy G.D. Hester, Manos M. Tentzeris
School of Electrical and Computer Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332–0250
Email: jimmy.hester@gatech.edu

Yunnan Fang
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332–0250
Email: yfang6@mail.gatech.edu

Abstract—In this paper, we report the most sensitive inkjet printed reduced graphene oxide based ammonia sensor as well as the first inkjet printed carbon nanotube based dimethyl methylphosphonate (DMMP) vapor sensor to date. The processes utilized to fabricate the sensors, including substrate surface modification, inclusion of porosity enhancing nanospheres and chemical functionalization, are outlined. The testing set-up and protocols are described and finally the measurement results are shown with displayed sensitivities of 8.5% for 30 ppm of ammonia and 5% for 2.5 ppm of DMMP. These results may set the foundation for fully inkjet printed, conformal, ‘zero-power’ and low cost ubiquitous wireless multi-gas motes.

I. INTRODUCTION

As 2D structure based nanomaterials, carbon nanotubes (CNTs) and graphene have been and still are attracting a lot of interest due to their unique physical and chemical properties. On top of their semiconducting or extremely high intrinsic conductivities (depending on their chirality and size), their ability to change electrical properties after absorption of chemical species [1] has been applied for resistometric gas analyte detection.

A few processes can be utilized to fabricate components with carbon nanostructure materials ; the most common one being the use of chemical vapor deposition (CVD) to grow the carbon nanostructures on the locations previously covered by a metal catalyst. However, this process requires heating the substrates to about 1000 °C, which is not a temperature that flexible substrates can withstand. For these substrates, it is advantageous to utilize printing methods, as they deposit previously synthesized nanomaterials that have been dispersed into a solvent. Inkjet printing is one of the most versatile printing methods for this application.

For these reasons, the use of inkjet printed carbon-based nanomaterials on low cost flexible substrates has attracted a substantial amount of interest for low cost, flexible, ubiquitous, sensitive, reusable and very responsive wireless chemical sensors for Internet of Things (IoT) motes and Smart Skins (SS) [2]. Integration of these printed materials into inkjet-printed conformal motes has already been reported [3], [4]. However, the application of inkjet-printed CNTs to detect other gases

than ammonia and the use of inkjet-printed graphene (that is cheaper than CNTs and that does not suffer from chirality dependent properties, contrary to CNTs) still are rather unexplored areas.

In this paper, we report the most sensitive fully inkjet-printed reduced graphene oxide (rGO) ammonia sensor. We also demonstrate the first fully inkjet printed CNT sensor for DMMP detection. In Sec. II and Sec. III, we discuss the fabrication processes for both sensors, the testing system and followed protocol. We then report the measured performances of the rGO and CNT sensors in Sec. IV.

II. FABRICATION

Both of these sensors were printed on a 125 μm thick polyimide Kapton HN film from Dupont. All the printing was done using a Dimatix 2831 inkjet printer with DMC-11610 10 pL cartridges.

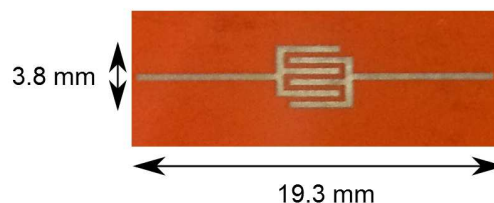


Fig. 1. Fully inkjet printed carbon nanomaterial-based sensor on Kapton HN flexible polymer substrate

A. rGO sensor

1) *GO ink*: The graphene oxide ink was prepared by dispersing nano graphene oxide powder (90 nm diameter flakes) from Graphene Supermarket (Reading, MA, USA) and commercially available negatively charged (carboxyl-terminated) polystyrene nanospheres into water. Glycerol was used as a co-solvent to increase the viscosity to about 10 cP, in the range of optimal viscosity values for inkjet inks. The ink was then sonicated to ensure good dispersion of the particles in the solvent.

2) *Surface modification of the polyimide film*: The Kapton was first surface modified, with the process described in [4], in order to make the surface more hydrophilic and therefore improve the printing quality of water based inks. This was done by introducing a layer of positively charged particles (such as amine groups) on the surface of the film and then utilizing a layer-by-layer dendritic amplification process to increase the density of surface groups. This process was repeated as many times as necessary in order to get high enough charge density at the surface of the polyimide film.

3) *Printing and reduction process*: Between 5 and 30 layers of the previously described GO ink were then inkjet printed onto the substrate in order to deposit square patches of graphene oxide nanoparticles. The ink was carefully and slowly dried at 90 °C for 5 hours in order to obtain as uniform a particle deposition as possible. The samples were then put in a vacuum oven at 100 °C for 10 hours in order to remove the potentially left-over glycerol. The GO films were subsequently washed with acetone to remove the polystyrene nanospheres before the printed GO flakes were reduced at 300 °C for 1 hour in an atmosphere of 98% of N₂ and 2% H₂ in order to obtain patches of reduced graphene oxide (rGO).

Finally, interdigitated electrodes (IDEs), with 4 mm long and 350 μm wide fingers separated by 350 μm wide gaps, (Fig. 1) were fabricated by printing 5 layers of commercial silver nanoparticle ink, from Suntronic, before drying them and sintering the silver nanoparticles in an oven at 110 °C for 3 hours.

B. CNT sensor

1) *CNT ink*: CoMoCAT CG300 single wall CNTs (SWCNTs) from SouthWest NanoTechnologies, were dispersed in Dimethylformamide (DMF) and sonicated with a probe sonicator. Increasing concentrations were tested to find the highest concentration that offered good dispersion of the CNT and stability of the ink over time. This maximum concentration, 25 mg L⁻¹, was then used in the final CNT-based ink.

2) *Printing*: Between 5 and 30 layers of the previously described CNT ink were then inkjet printed onto the substrate to deposit square CNT patches. The ink was left to dry at room temperature before the samples were put into a vacuum oven at 100 °C for 10 hours to remove the potentially left-over DMF. Some of the inkjet printed CNT films were then *functionalized* with carboxyl, amine or hydroxyl groups or a hexafluoroalcohol (HFA) via a series of reactions that have been reported in [5], [6], [7]. Finally, the electrodes were printed the same way as the ones for the rGO sensors.

III. SENSOR TESTING

A. Experimental set-up

A Flexstream gas standard generator from KIN-TEK was used to generate controlled concentrations of analytes in a carrier gas. Here, we used ultra pure nitrogen for that purpose. This system utilizes permeation tubes that have a set permeation rate for the analyte gas - the tube permeates the analyte into the diluent gas. The concentration is therefore

inversely proportional to the output flow rate. A custom-made gas chamber (Fig. 2) was fabricated to confine the sensors during the gas exposure tests. The chamber is fed through one end by the output of the Flexstream and the gas is exhausted through a small tube at the other end of the box. Cables are brought into the box in an airtight fashion and connect the leads of the electrodes to an Agilent 34401A digital multimeter.

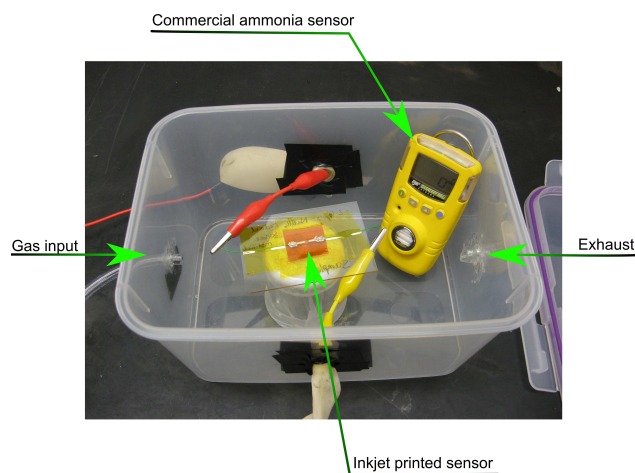


Fig. 2. Test enclosure including the tested inkjet printed sensor and the commercial ammonia reference gas sensor

B. Experimental protocol

Pure nitrogen was fed into the sealed environment for 30 min in order to chase the air out and induce the desorption of potential chemical species previously absorbed by the nanomaterial. The flow rate used here was the same as the one that would then be used to generate the desired analyte concentration. The desired analyte concentration was then fed into the box and the resistance values of the sensor recorded.

IV. MEASUREMENT RESULTS

A. rGO ammonia sensor

The results for a 10 GO-ink-layers rGO sensor are shown on Fig. 3. The plot displays the relative sensitivity of the sensors that is defined as

$$S(t) = \frac{R(t) - R(t_0)}{R(t_0)} \quad (1)$$

where $S(t)$ is the relative sensitivity of the sensor at time t , $R(t)$ is the resistivity of the sensor at time t and $R(t_0)$ is the resistivity of the sensor at the reference 'starting' time t_0 . This sensitivity is compared with the recorded concentration of a commercial ammonia detector from BW Technologies. On the plot of Fig. 3, the reference time was taken at $t_0 = 0$. The sensors displayed a maximum response of about 8.5% with a response time of 20 minutes for an ammonia concentration of less than 30 ppm. With more than 2.8%/10ppm, this makes it the most sensitive inkjet printed rGO ammonia sensor compared to the state of the art of about 2.1%/10ppm [8]. The

absorption rate of the gas by the rGO decreases as more has been absorbed and eventually making the sensitivity saturate at its maximum value for that concentration. The ammonia feeding having been stopped before complete saturation of the sensitivity, the intrinsic maximum sensitivity of the sensor is actually higher than measured here. The responses from the rGO sensor and the commercial sensor are very similar during the first 20 minutes. This shows that the response time of the inkjet printed sensor is very comparable to that of a commercial ammonia sensor. The major difference between the performance of the two sensors is the desorption capability. In this configuration, the rGO sensor does not come back to its original state after sensing, and a second exposure (to about 10 ppm) only induces a small response from its new baseline resistance. Inkjet printed heater solutions are now being developed to heat the sensor after exposure in order to trigger a complete and fast desorption.

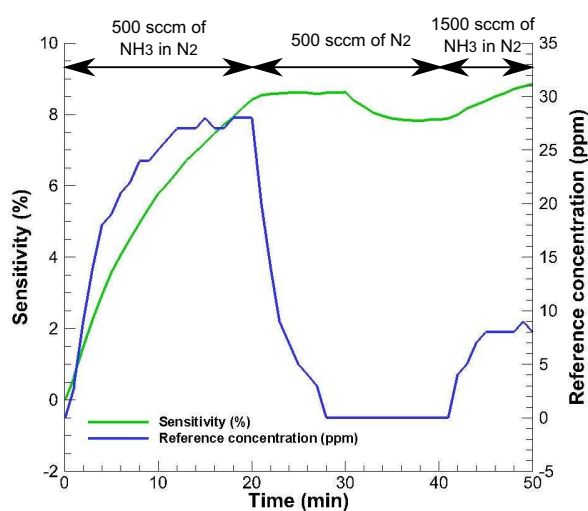


Fig. 3. Measured sensitivity response of the rGO ammonia sensor (green) and reference concentration measured by a commercial ammonia sensor (blue)

B. CNT DMMP sensor

Measurements were taken with 5 sensors printed with 20 layers of CNTs, and each one of them functionalized with a different chemical group. One functional group (HFA) stood out, as its sensitivity was one order of magnitude higher than that of all the other functionalized and bare CNTs. This functional group was therefore then applied to all subsequent sensor prototypes.

An inverse dependency of the sensor sensitivity with the number of layers was also observed. The measurement data of an HFA-functionalized 10 layer sensor is shown on Fig. 4. At the 15 minutes mark after the beginning of the exposition to DMMP, the 10 layer sensor displayed about a 2.5% sensitivity compared to the 1.2% of the 20 layer sensor. With less than 10 layers, the resistivity of the sensor became too high to measure. This decrease in sensitivity with increasing CNT

amount is attributed to the reduced availability of some of the CNTs for interaction with the surrounding gas, as the thickness of the film increases. It is difficult for the gas analyte to interact with the CNTs that are at the bottom of the printed layer. However, these “buried” CNTs still contribute to the conductivity of the film, therefore reducing the overall sensitivity of the resistometric sensor.

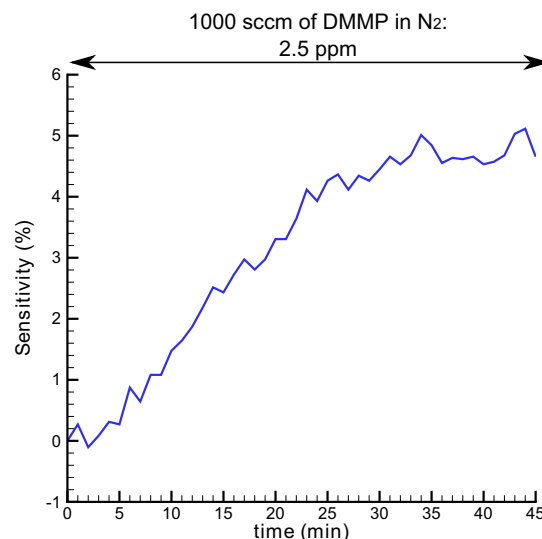


Fig. 4. Measured sensitivity of an HFA-functionalized 10 layers inkjet printed CNT sensor

This CNT sensor is, as far as we know, the first inkjet-printed functionalized CNT-based DMMP sensor ever reported.

This CNT sensor was developed specifically for the detection of DMMP. However, this work is only one example of a technology with a much broader scope. Indeed, the CNTs only serve as a conductive template that is then chemically functionalized to target one specific gas. As a consequence, the use of functional groups to increase the sensitivity and selectivity of CNT-based sensors can be utilized to form an array composed of differently functionalized sensors capable of sensing and recognizing a wide range of gases [9]. Integrated into a wireless system, this gas sensing “Smart Skin” would be able to offer a unique “Wireless Sensing Signature” associated to each gas, for a wide range of detectable gases and environments.

V. CONCLUSION

In this work, we have reported the fabrication of the most sensitive inkjet printed rGO based ammonia sensors as well as the first inkjet printed CNT based DMMP sensor to date, and achieved sensitivities of, respectively, 2.8%/10ppm and 20%/10ppm. These results are very encouraging and the performance of sensors fabricated with non-flexible-substrate-compatible methods [10] show that the room for improvement is still significant. Judging by these results, further efforts in this direction could potentially give birth to a new generation

of flexible, ubiquitous, low cost, wireless gas sensors arrays capable of communicating a “Wireless Sensing Signature” specific to each of a wide variety of detectable gases. These components offer tremendous potential for wide coverage wireless gas sensing, with applications in the areas of the Internet of Things (IoT) and “Smart-Skins” and “Smart-House” topologies.

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REFERENCES

- [1] F. Schedin, A. Geim, S. Morozov, E. Hill, P. Blake, M. Katsnelson, and K. Novoselov, “Detection of individual gas molecules adsorbed on graphene,” *Nature materials*, vol. 6, no. 9, pp. 652–655, 2007.
- [2] M. Tentzeris and L. Yang, “Inkjet-printed paper-based RFID and nanotechnology-based ultrasensitive sensors: The green ultimate solution for an ever improving life quality and safety?” in *Next Generation Society. Technological and Legal Issues*. Springer, 2010, pp. 55–63.
- [3] C. Occhiuzzi, A. Rida, G. Marrocco, and M. Tentzeris, “RFID passive gas sensor integrating carbon nanotubes,” *IEEE Trans. Microw. Theory Tech.*, vol. 59, no. 10, pp. 2674–2684, 2011.
- [4] T. Le, V. Lakafosis, M. M. Tentzeris, Z. Lin, Y. Fang, K. H. Sandhage, and C.-p. Wong, “Novel techniques for performance enhancement of inkjet-printed graphene-based thin films for wireless sensing platforms,” in *2013 European Microwave Conf. (EuMC)*. IEEE, 2013, pp. 17–20.
- [5] S. C. Davis, V. C. Sheppard, G. Begum, Y. Cai, Y. Fang, J. D. Berrigan, N. Kröger, and K. H. Sandhage, “Rapid flow-through biocatalysis with high surface area, enzyme-loaded carbon and gold-bearing diatom frustule replicas,” *Advanced Functional Materials*, vol. 23, no. 36, pp. 4611–4620, 2013.
- [6] G. Wang, Y. Fang, P. Kim, A. Hayek, M. R. Weatherspoon, J. W. Perry, K. H. Sandhage, S. R. Marder, and S. C. Jones, “Layer-by-layer dendritic growth of hyperbranched thin films for surface sol-gel syntheses of conformal, functional, nanocrystalline oxide coatings on complex 3d (bio) silica templates,” *Advanced Functional Materials*, vol. 19, no. 17, pp. 2768–2776, 2009.
- [7] Y. Fang, V. W. Chen, Y. Cai, J. D. Berrigan, S. R. Marder, J. W. Perry, and K. H. Sandhage, “Biologically enabled syntheses of freestanding metallic structures possessing subwavelength pore arrays for extraordinary (surface plasmon-mediated) infrared transmission,” *Advanced Functional Materials*, vol. 22, no. 12, pp. 2550–2559, 2012.
- [8] V. Dua, S. P. Surwade, S. Ammu, S. R. Agnihotra, S. Jain, K. E. Roberts, S. Park, R. S. Ruoff, and S. K. Manohar, “All-organic vapor sensor using inkjet-printed reduced graphene oxide,” *Angewandte Chemie International Edition*, vol. 49, no. 12, pp. 2154–2157, 2010.
- [9] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Dai, S. Peng, and K. Cho, “Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection,” *Nano Letters*, vol. 3, 2003.
- [10] J. Novak, E. Snow, E. Houser, D. Park, J. Stepnowski, and R. McGill, “Nerve agent detection using networks of single-walled carbon nanotubes,” *Applied physics letters*, vol. 83, no. 19, pp. 4026–4028, 2003.