Novel Techniques for Performance Enhancement of Inkjet-Printed Graphene-Based Thin Films for Wireless Sensing Platforms

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***Abstract*— In this paper, we present various novel techniques for the performance enhancement of nanotechnology-enabled wireless platforms utilizing inkjet-printed carbon-based thin films, especially for gas sensing applications. The key advancements include surface modification techniques to drastically reduce film thickness (from micron to nm) and a unique in-house developed nano-patterning process to increase porosity of the thin film resulting in increased surface contact area with gas. We have improved the performance by nearly one order of magnitude (a factor of around 10), increasing the sensitivity to 4.8% at 60 ppm, compared to previously reported results (6% sensitivity after exposure to 500 ppm NH_3). We also propose a novel technique for carbon-based material growth on top of pre-printed patterns. The proposed graphene-based thin film approach could set the foundation for a plethora of novel wireless sensing and gas-reconfigurable communication platforms.**

Keywords — Graphene oxide, wireless gas sensor, inkjet-printing technology, surface modification, nano-engineering.

I. Introduction

Over the last decade, there have been numerous breakthroughs in sensing and wireless technologies due to the continuous advances in the area of nanostructures, such as carbon nanotubes (CNTs) and graphene. A topic of substantial interest in both industry and academia is the development of techniques to produce low-cost, scalable, sensitive and reusable wireless sensors for Internet of Things, smart skin and M2M applications. Efficient and reproducible techniques allowing for the easy integration of nano-materials have become one of the critical steps during the fabrication process through recent materials science advances[1-3]. Meanwhile, the use of low-cost inkjet printing techniques for the development of carbon-based thin films as a sensing medium, and their integration into wireless sensor nodes has been reported[4,5]. Based on those previous efforts, we have identified several key areas of exploration for performance enhancement of the wireless platforms utilizing inkjet-printed reduced graphene oxide (rGO) thin films. In particular, this paper focuses on improving the performance of novel gas sensors, with an emphasis on film thickness, porosity, and uniformity, while taking advantage of low-cost large-area inkjet-printing fabrication processes.

Namely, the contributions of this paper include:

1) Surface Modification of the Substrate: Via proprietary in-house developed processes, we modify the substrate so that the graphene platelets bind to the surface in an even manner, approximately one molecule thick. This approach greatly reduces the film thickness and increases the uniformity.
2) Nano-sphere-based Porosity Enhancement of the Thin Film: Via nano-engineering of the thin film during processing, we are able to increase and control precisely the porosity of the thin film, thus enhancing sensitivity to gases.

II. Novel Techniques For Performance Enhancement

A. Surface Modifications

Based on our previous sensor efforts, it became clear that in order to enhance the weak binding between the water-based GO ink and typical low-cost substrates, new techniques have to be developed that enhance the film patterning, uniformity, and reduce the film thickness, which helps time consulting and lower cost. For the purpose of producing uniform (root-mean-square roughness less than 50 nm) and ultra-thin (average thickness less than 100 nm) carbon films, an in-house developed surface engineering process which had been previously used to enhance the wettability of Si wafers[6], was utilized to pretreat flexible substrates (such as PET and Kapton) prior to GO ink deposition. The wettability and printability of the GO ink on the substrate were dramatically improved after the surface modifications. As a result, agglomerations and islanding effects were avoided and it became possible to inkjet print conformal, continuous, and ultra-thin (< 50 nm thickness) GO films on numerous substrates spanning from conventional Si wafer and glass to low-cost flexible substrates such as Kapton and PET.

The process employed in this work for substrate surface modifications includes: (1) Positively charged chemical groups (such as amine groups) were first introduced to the substrate surfaces. (2) Through a well-established layer-by-layer dendritic amplification, these groups are amplified to the desired density (Figure 1). The resulting substrate surfaces became densely positively charged and hydrophilic, and ready for conformal inkjet printing of the negatively charged and hydrophilic carbon-based nanomaterials. The opposite charges created a strong electrostatic force which attracts and bonds the graphene platelets in exactly the desired printing pattern. Combining this process with lithographic or masking techniques, the width resolution of the printing process can be advanced down to a few um (<5 um), ideal for the purpose of inkjet printing graphene traces for electrical circuits on virtually any surfaces ranging from organics to glass and silicon wafers.

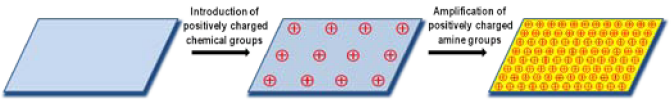

Figure 1. Process of surface modifications to a flexible substrate

The enhancement of printability of water-based GO ink to surface modified Kapton was dramatic. As shown in Figure 2, water-based GO ink tended to agglomerate on surface of un-modified Kapton. Substrate surface modifications drastically improved the printability of GO ink to the substrate, as indicated by the precisely controlled shapes and their clean and sharp edges.

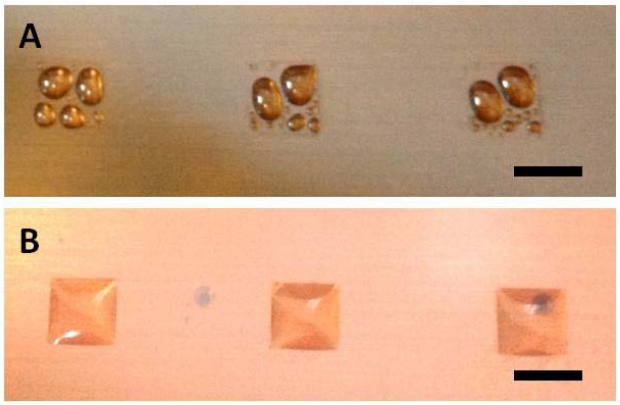

Figure 2. Optical images of inkjet printed GO ink (5 passes) on surface unmodified (A) and modified (B) Kapton substrate. Scale bars: 3 mm.

Indeed, a contact angle analysis showed that the surface modifications to Kapton substrate significantly enhanced the wettability of water on the substrate, as indicated by the drastic reduction of contact angle of water from about 88 degree (on surface of unmodified Kapton. Figure 3A) to about 40 degree (on surface of modified Kapton. Figure 3B).

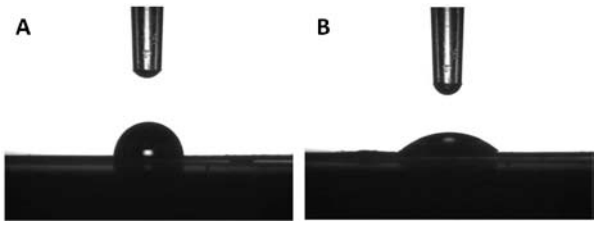

Figure 3. Contact angle analyses of water on surface un-modified (A) and modified (B) Kapton substrates. The contact angles of water on surface unmodified and modified Kapton were about 88 and 40 degree, respectively.

B. Porosity-creating Techniques

The specific surface area of the nanomaterials-based sensors is critical to their molecule level sensitivity to various agents. In order to increase the specific surface area, we prepared a highly porous thin film utilizing a novel porosity-creating technique that created nanoscale pores in the thin films via the introduction and selective dissolution of commercially available, low-cost polymer nanospheres made of polystyrene.

Briefly, GO particles were treated with polyethylenimine to bear surface amine groups, and the positively charged GO particles were then mixed with carboxyl-terminated polymer nanospheres and let bind via electrostatic interaction. Water-based inks were then prepared from the nanosphere-bound GO and the viscosity of the resulting suspensions was adjusted with glycerol to optimize their printability on a Dimatix DMP-2800 inkjet printer. After the evaporation of glycerol and water in a 80 °C oven, the printed thin films were sequentially incubated first with acetone and then with toluene to selectively remove the polystyrene nanospheres. As a result, high porous GO thin films on Kapton substrate were created in Figure 4.

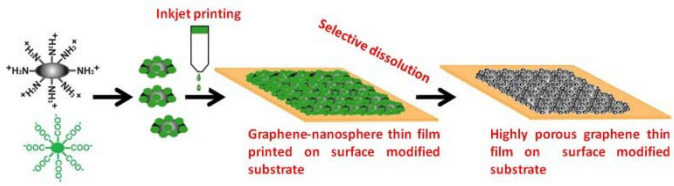

Figure 4. Inkjet printing of highly porous carbon-based nanomaterials on a surface modified flexible substrate.

Figure 5 shows the morphological difference between inkjet printed graphene oxide thin films on Kapton substrates with and without the introduction of polymer nanospheres. Figure 5A shows an SEM image of the highly porous GO film prepared with the introduction of polymer nanospheres, while Figure 5B showing the traditionally prepared GO film without the involvement of polymer nanospheres. The introduction of polymer nanospheres substantially increased the porosity of the GO thin film.

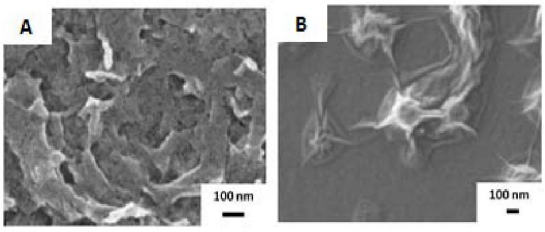

Figure 5. SEM images of (A). a GO-polystyrene thin film printed on surface modified Kapton substrate (5 passes) after the selective removal of polymer nanospheres, and B). GO thin film printed without the presence of nanospheres in the ink (5 passes).

It has to be stressed that high porosity of a thin film typically deteriorates its conductivity. We are currently varying ink formulations and printing conditions (such as changing the size of the polymer nanospheres and the thickness of the thin film, and tuning the ratio of GO to nanosphere particles) to obtain the best compromise between the conductivity and porosity of the printed rGO thin films.

III. Battery-less Wireless Sensing and Communication Platform

In a way similar to that reported previously[4], we used the WISP sensing and communications platform to test the improvement of the wireless sensor sensitivity utilizing the above techniques. The WISP is a battery-free, fully passive, and programmable RFID Tag[7], which can be powered, and read by off-the-shelf EPC Gen2 UHF RFID Readers and has an on-board microcontroller for sensing and computing functions.

The WISP was a flexible platform offering the reliability of wireless digital transmission. The WISP-GS was solely powered by the RF energy illuminated by a very popular commercial RFID Reader. This 915MHz RF energy was rectified with its charge pump to charge the on-board capacitor. As soon as sufficient energy was accumulated and the voltage across the capacitor monitored by a supervisor exceeded the turn-on voltage of the MCU by an overhead margin, a regulated voltage of 1.805V is used to power both the MCU and our prototype external gas sensing board.

The external WISP-GS board consisted of the inkjet-printed rGO sensor, presented in the previous section, as well as the analog interface of this sensor.

The analog interface was essentially a voltage divider, in which the voltage drop across the gas sensor module was directly tied to the resistance change of the sensor's graphene film pad and could easily be captured with the WISP's integrated analog-to-digital converter (ADC) (pin 2.3). The resolution achieved can be defined by dividing the maximum resistance value by the 1024 discrete levels of the integrated 10-bit ADC, which gives approximately ± 1 mV accuracy.

Our modified WISP graphical user interface can report in real time the resistance of the rGO film that can be easily mapped to the real gas concentration with the extracted fitting equation, the sensor's serial number and type, the total number of readings, the time it was last seen as well the full EPC Gen2 message transmitted. The report rate is only a few milliseconds, allowing for immediate reaction to health-threatening gas concentrations.

VI. Gas Sensing Setup

To test and validate the rGO film enhancements, we examined the samples with printed rGO on Kapton substrate under gas tests. The measurement setup and procedures used here are identical to the timing tests given in [4, 5]. We used a KIN-TEK FlexStream™ Gas Standards Generator to provide a stable gas source with accurate concentrations. The rGO thin film was placed in a custom designed gas chamber under influence of the test gas. The process consists of: 1). Placing samples in a custom enclosure and flowing pure Nitrogen on the sample for 5 minutes to cleanse it, and 2). Introducing the test gas (NH_3 in this case) at the desired concentration and beginning measurements every minute until near saturation condition was achieved.

V. Results

A. Thin film Profile Reduction

By the use of substrate modification, we were able to substantially reduce the thin film thickness. Table 1 provides the results of the thickness measurements taken with a DekTak® profilometer for thin films consisting of 1-5 layers of reduced graphene oxide.

TABLE I
Profile Measurements of RGO thin films

Layers	**1**	**2**	**3**	**4**	**5**
Thickness [nm]	54.0	93.3	144.8	202.0	245.1
Avg. Thickness per Layer [nm]	54.0	46.7	48.3	50.5	49.0

Note that the average thickness per layer on the treated substrate is only 49.67 nm. In previous efforts, at least 15-20 layers were required to achieve a conductive medium. Using the methods given here, we can obtain a conductive medium with just 1 layer. We can then print films as thin as 50 nm.

B. Gas Test Measurements

Figure 6 provides the results of a recent gas test measurement using the new rGO thin films developed on the treated Kapton. Here, we will define a metric of performance called sensitivity S, which is the normalized resistance change as in

$$S=(R_{gas} - R_{air}) / R_{air} \times 100\% \quad (1)$$

Note that here we achieve nearly 5% sensitivity change in response to 60 ppm NH_3. This is a substantial improvement on our previous result of 6% with 500 ppm NH_3. Hence, we have achieved a near 10-fold improvement in sensitivity via thin film thickness reduction and uniformity enhancements.

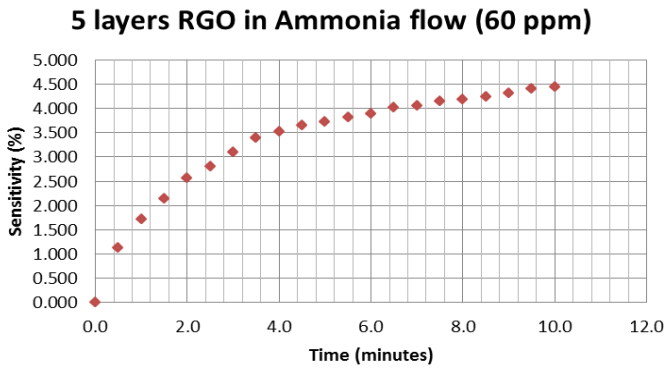

Figure 6. Sensitivity of the improved rGO thin film.

VI. Conclusion

In this work, we have demonstrated the efficacy of various novel approaches to enhance the quality of inkjet-printed rGO thin films. Through all these novel techniques, we have succeeded in reducing the thickness of inkjet-printed graphene thin film by an order of magnitude (micron to nm), substantially increased film uniformity, and reduced process variance across the board.

In addition, we dramatically improved the sensing performance of our wireless sensing platforms based on these films. It must be noted that we have demonstrated a 10-fold improvement in sensitivity using the substrate modification technique alone, and we are expecting further enhancement through the modification of the nano-sphere patterning and GO ink. The proposed approach could set the foundation for the development of a completely new class of nanotechnology-enabled wireless sensing and gas-reconfigurable communication devices combining the advantages of ultra low cost inkjet printing with the unique sensing capabilities of rGO thin films.

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