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HIGHLY SENSITIVE NO₂ GAS SENSORS BY SPARK ABLATION ON CVD GRAPHENE

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ABSTRACT

This work reports, for the first time, the use of spark ablation with impaction printing to selectively deposit silver (Ag) and gold (Au) nanoparticle (NP) functionalization on single-layer graphene (SLG) based gas sensors. This method avoids lithography and chemical processes, maintaining the device's quality while potentially lowering the fabrication costs. Ag-decorated sensors reveal a three-fold improvement in nitrogen dioxide (NO₂) gas response over pristine-SLG sensors. We demonstrate detection capabilities down to 50 ppb at room temperature, negating the requirement for external thermal or photoactivation. In contrast to pristine or Au-decorated SLG sensors, Ag-decorated devices exhibit 96% recovery at room temperature (RT). These results highlight the potential of using spark ablation with impaction printing for functionalizing graphene-based sensors.

KEYWORDS

Gas sensors, CVD-graphene, functionalization, nanoparticles, spark ablation.

INTRODUCTION

Graphene, a remarkable two-dimensional material, has been extensively investigated for gas-sensing applications due to its inherently low electronic noise [1] and exceptional sensitivity down to the single molecule level [2], which makes it a promising candidate for gas-sensing applications. However, graphene-based gas sensors suffer from poor recovery [3] and cross-sensitivity [2]. The first issue can be resolved using ultraviolet light irradiation [4] or thermal treatment [5]. For cross-sensitivity issues, graphene can be functionalized, providing either defects or functional groups that can be more specific to certain gases [6]. By creating an array of functionalized sensors, a device can be realized with better selectivity than a single gas sensor.

Researchers often functionalize chemical vapour deposition (CVD) graphene surfaces using sputtering or pulsed laser deposition (PLD) techniques [7], [8]. These techniques are well-suited for modifying the surface of single gas sensors. While creating gas sensor arrays, multiple lithography steps are required to selectively functionalize different parts of the device. These processes are not only time-consuming but degrade the graphene quality over repeated lithography cycles by leaving residues or causing damage to the graphene.

Ideally, subsequent functionalization steps should not impact existing functionalization layers when creating such an array. To tackle this problem, this work aims to functionalize the graphene surface using a fully dry

approach, i.e., without any chemical precursors and waste production. It is based on the spark ablation technique [9] with impaction printing to decorate metallic (Ag and Au) nanoparticles on the desired location of the SLG-based sensors.

EXPERIMENTAL SECTION

Device fabrication

Commercial single-layer CVD graphene devices were fabricated by Graphenea using a combination of standard semiconductor techniques, such as photolithography, etching, and Au contact metal deposition on an oxidized Si wafer.

Fig. 1 shows the equipment to generate the NPs and print them onto a target sample at RT. The VSP-P1 nanoprinter (VSParticle B.V.) contains a VSP-G1 (VSParticle B.V.) equipped with high-purity electrodes to generate nm-size Ag and Au-NPs on the sample's surface. This method utilizes sparks generated between two opposing metal electrodes placed with a gap of 1 mm between them within the air-tight chamber. Pure argon, flowing at a rate of 1 L/min, was used as a carrier gas. The generated aerosol-containing NPs are flown through a nozzle ($\varnothing=0.1$ mm) located in a chamber at RT and 0.15-0.2 mbar pressure. The pressure difference between the generator and the low-pressure chamber (where the sample is placed) leads to an aerosol acceleration impacting the NPs onto the target substrate. Precise local printing is enabled by moving the stage with speeds from 1000 $\mu\text{m}/\text{sec}$ to 3000 $\mu\text{m}/\text{sec}$, while utilizing the spark voltage and current as 1kV and 3.5mA, respectively. In the system, 90% of the generated NPs are removed via a secondary bypass flow to the vacuum pump before impaction.

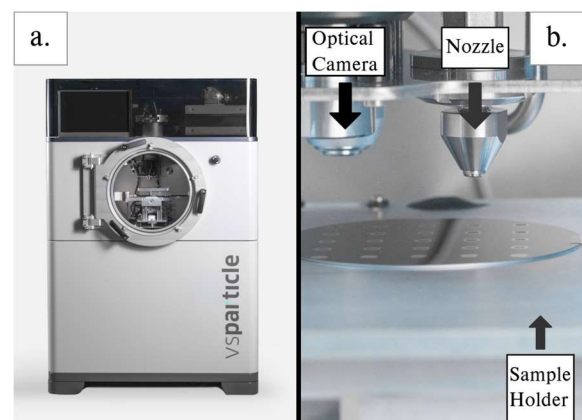


Figure 1: VSP-P1 nanoprinter system (VSParticle B.V., Netherlands) utilized for NP printing onto SLG graphene devices.

Material characterizations and device testing

A Scanning Electron Microscope (SEM) Hitachi Regulus 8230 is utilized to check the morphology of the NP deposition. Raman Spectroscopy was employed using a Renishaw in Via Raman microscope with a 633 nm laser to monitor the graphene quality before and after the NP decoration. Electrical measurements were conducted on a semi-automatic probe station with a semiconductor parameter analyzer to examine the electrical behaviour of the devices.

The gas sensing measurements were carried out inside a sealed stainless steel chamber to ensure controlled testing conditions. Target gases were accurately produced employing an Owlstone V-OVG system, including a NO₂ permeation tube and ultra-high-purity (99.999%) N₂ as a carrier gas. Electrical characterization was carried out using a dual-channel Keithley 2612B Source Measure Unit (SMU) for high-precision current-voltage measurements using a two-point probe approach. An Agilent 34970A data acquisition system with a 34901A multiplexer module was utilized to provide time-multiplexed switching, which allowed for the characterization of multiple devices on a single sample. An automation script built with LabVIEW was created to control data collection.

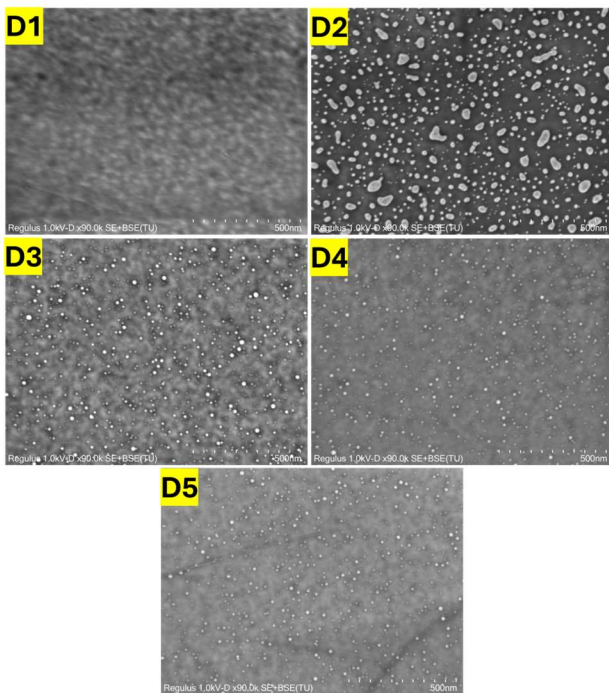


Figure 2: Top surface SEM images: (D1) pristine graphene, (D2) after Au-NPs decoration with an area coverage of 15.5%, and after Ag-NPs decoration with an area coverage of 3.5% (D3), 2% (D4) and 0.8% (D5), respectively. The coverage was extracted using ImageJ.

RESULTS AND DISCUSSION

All six graphene-based sensors were decorated utilizing impaction printing methods based on spark ablation using different stage speeds. Out of them, three Ag-NP devices were prepared with varying surface coverages: 3.5% (at a stage speed of 1000 $\mu\text{m}/\text{sec}$), 2% (at 2000 $\mu\text{m}/\text{sec}$), and 0.8% (at 3000 $\mu\text{m}/\text{sec}$). These devices

were labeled as D3, D4, and D5, respectively. Similarly, three devices were printed for Au-NPs. However, Au-NP decorated devices did not show any response against the NO₂ gas. Therefore, only one Au device, labelled D2, is shown for comparison. Additionally, one device without any NP deposition was measured (D1). SEM examined surface morphology before (D1) and after Au & Ag -NP decoration (D2-D5) on the graphene-based devices are shown in Fig. 2.

To assess film quality and uniformity, Raman Spectroscopy was utilized on multiple points across the graphene surface before and after NP decorations for all the devices. The Raman spectrum shows a characteristic D peak at 1325 cm^{-1} , G peak at 1590 cm^{-1} , and 2D peak at 2643 cm^{-1} . The I_{2D}/I_G intensity ratio and FWHM (2D) were calculated as 1.73 and 31.3 cm^{-1} , demonstrating SLG with fewer defects [10]. The Raman spectra remained consistent for all measured points, and the absence of peak position shift after NP deposition confirms that graphene quality remains the same across the surface for all the devices. Fig. 3 represents the Raman spectra only for one single-point measurement per sample.

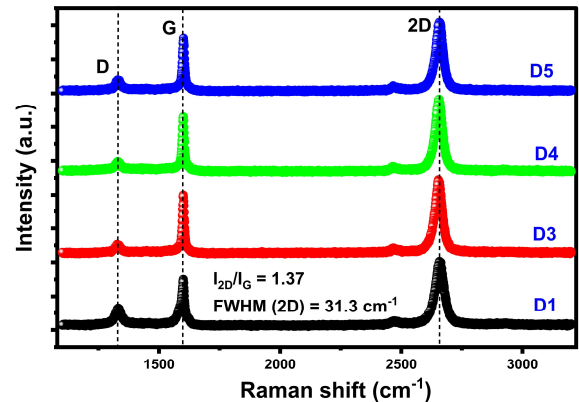


Figure 3: Raman spectroscopy characterization of all four devices using a 633 nm laser. The absence of changes in the D/G ratio indicates no damage due to printing. From the 2D peak, it can be concluded that SLG is present.

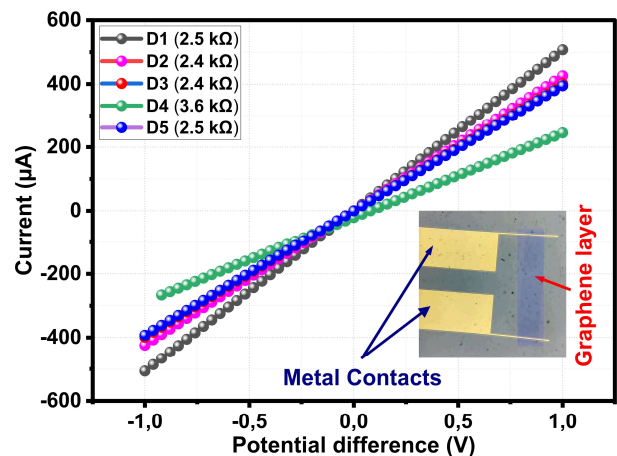


Figure 4: I-V characteristic of all devices with dimensions of 1000 \times 200 μm as shown in the inset. The devices display Ohmic behaviour. Furthermore, the functionalization has no measurable impact on the resistance.

Furthermore, electrical measurements were conducted in the ambient to determine graphene's electronic transport properties before and after the NP decoration. To obtain the I-V characteristic, two probe measurements were performed on the graphene layer for all the devices (Fig. 4). The linear response between graphene and metal contact indicates the ohmic behaviour of the devices. Before and after NP decoration, there is only minimal change in the resistance of the devices, indicating no major impact of NP printing on the graphene quality.

Lastly, gas-sensing measurements were performed against 1 ppm NO₂ gas at 80°C under 1V constant voltage bias using 99.999% N₂ gas as a carrier for all the sensors (Fig. 5, top). Since typical graphene, under ambient conditions, behaves as a p-type semiconductor, it inherently possesses an abundance of holes. When NO₂ (a strong electron-withdrawing gas) comes into contact with the graphene surface, it removes the free electrons, making graphene more p-type. As a result of this interaction, the material experiences a detectable drop in resistance as NO₂ molecules physisorbed onto the surface.

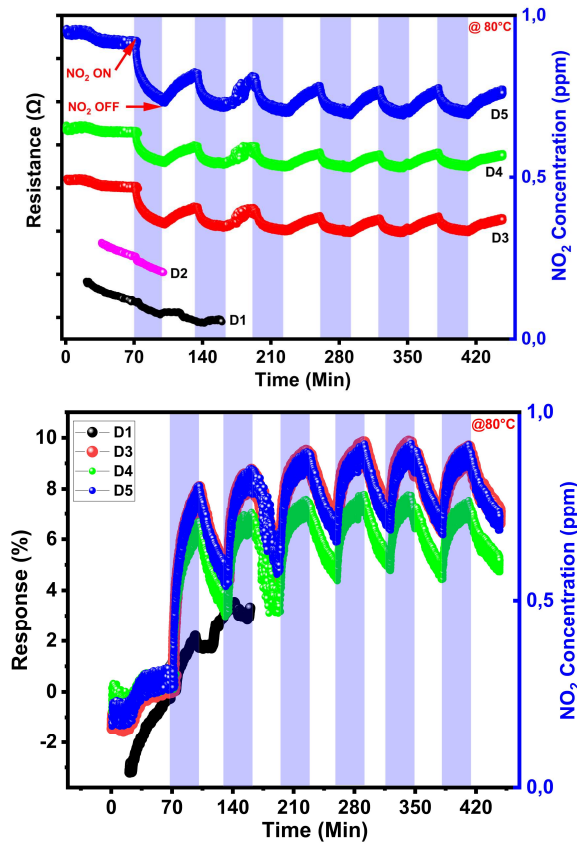


Figure 5. NO₂ gas sensing behaviour of all five sensors. Top: repeatability of the sensing devices towards 1 ppm NO₂ pulses (shaded area) with the chip at 80 °C. Bottom: Calculated response of the sensing film for all devices.

Fig. 5 (bottom) illustrates the response of all devices, determined using Eq (1). Here, R_{gas} denotes the resistance when the target gas is injected, and R_{air} represents the resistance before the first NO₂ pulse.

$$\text{Response (\%)} = \left\{ \frac{R_{air} - R_{gas}}{R_{air}} \right\} \times 100 \quad (1)$$

During the gas sensing measurements, pristine SLG (D1) is exposed to an N₂ atmosphere and subsequently to NO₂ for 30 minutes. The sensor's resistance significantly decreased when NO₂ was introduced and exhibited an average response for all the cycles of 2.2%. However, the device showed scarce recovery once the NO₂ flow was stopped, failing to restore to its initial resistance stage. Despite being exposed to pure nitrogen for 90 minutes, the sensor did not completely return to its initial state without further stimulated desorption processes. The incomplete recovery of D1 may be due to the higher binding energy between the graphene film and NO₂ gas molecules [11].

Furthermore, we studied the behaviour of functionalized devices (D2-D5). Interestingly, Au-decorated SLG (D2) didn't respond towards NO₂. One possible reason could be the difference in size and coverage area of the NPs. SEM measurements confirmed that the Au-NPs were notably bigger than the Ag-NPs (Fig. 2). Smaller NPs typically show higher reactivity as they have a higher surface-to-volume ratio and increased density of active sites for gas adsorption [12]. Besides this, the coverage area for Au-NPs is calculated as 15.5%, which is significantly higher than that of Ag devices. The excessive coverage area prevents gas molecules from interacting with the sensor by blocking adsorption sites [13]. This effect restricts gas adsorption and lowers charge transfer efficiency. Therefore, the size difference or high NP coverage could impact their sensing performance.

On the contrary, Ag-NPs functionalized devices, D3, D4 and D5, have an average response of 5.94%, 6.14%, and 5.22%, respectively, indicating an almost three-fold enhancement in response compared to pristine SLG (D1). Ag-NPs donate electrons to graphene since Ag (4.3 eV) has a lower work function than graphene (4.7 eV), which facilitates the electron transfer process, causing it to become less p-type doped. This transfer mechanism improves the device's response by increasing the active adsorption sites and, at the same time, their enhanced affinity towards a target gas [14], [8].

As observed, there is no full recovery during the first cycle. This could be related to fabrication-related residues, such as polymer contaminants, which may impact the performance of sensors. These impurities could modify the surface chemistry or produce strong adsorption sites, affecting the recovery behaviour. However, after the initial pulse, a 96% recovery was observed, which strongly contrasts with pristine SLG. This could be explained by reversible adsorption sites serving as sensing elements, and all irreversible adsorption sites have mostly been taken over.

Finally, Fig. 6 depicts the change in resistance of the D4 device using various NO₂ concentrations (50 – 1000) ppb at RT and 80°C. Compared to RT, the device at 80°C shows a higher baseline resistance and a more noticeable resistance decline during the NO₂ gas exposure, indicating that higher temperatures improve the efficacy of NO₂ adsorption and charge transfer. As a result, the device can detect NO₂ concentrations as low as 50 ppb, even at RT. The inset graph demonstrates the device's responses against NO₂ concentrations after the 1st NO₂ pulse, indicating that the sensor response rises with concentration and is consistently stronger at 80°C than RT. Interestingly, the

computed response at 80°C was 2.5 times greater as compared to RT, highlighting the considerable enhancement in gas response by temperature.

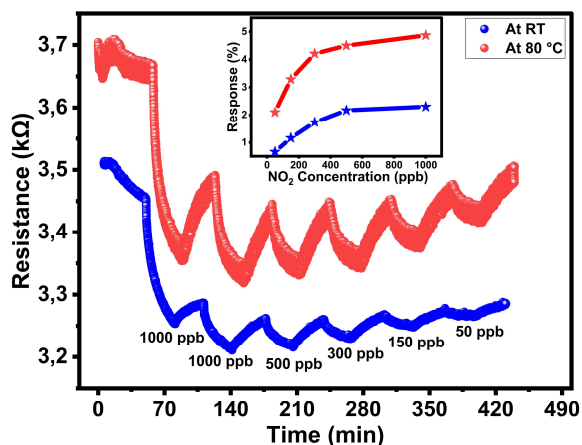


Figure 6: variation of resistance of device D4 at RT (blue) and 80°C (red) against different concentrations of NO₂, ranging from (50-1000) ppb. Inset: responses of the device vs. concentrations after the 1st NO₂ pulse.

CONCLUSION

We have demonstrated a novel approach to selectively functionalize Au and Ag-NPs on graphene-based gas sensors via a fully dry method utilizing spark ablation and impaction printing. Both SEM and Raman spectroscopy verified the successful integration of nanoparticles, with the latter showing no structural damage in the graphene after deposition. Ag-decorated devices exhibit a three-fold improvement in sensing performance with respect to pristine SLG, whereas Au-decorated devices showed no significant response to NO₂. Ag-decorated devices were able to detect NO₂ concentrations as low as 50 ppb while heating the device to 80 °C further enhanced the response. These findings highlight the potential of Ag nanoparticle modifications in boosting graphene-based gas sensors. Future research should concentrate on optimizing nanoparticle coverage and size to further improve sensor performance and selectivity.

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