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PYRENE DEPOSITION WITH A GFET-PV01

Application Note #4 from Paragraf's Technical Centre

Attaching of molecules, polymers or biomaterials to surfaces for sensing applications not only offers enhanced sensing properties over base substrates, but also allows for specific interactions to be probed.

One primary constraint when initially exploring these applications is the attachment of molecules to the inert materials typically chosen for sensing. Numerous methods have been trialled, with varying degrees of success. The use of pyrene derivatives to achieve this surface modification has perhaps been the most prevalent due to its simple procedure, mild reaction conditions and significant surface coverage.

Here, we present an optimised methodology for functionalising the exposed graphene surfaces of our GFET-PV01 devices with pyrenebutyric acid, which can be used as an anchor point for further attachment of primary amines or other nucleophiles via well-established EDC/NHS chemistry.

The GFET-PV01 is a research-focussed transistor with three electrode channels equally spaced around a large central gate – each distanced from one another to permit manual adjustment or adjustment with automated targeted deposition. Paragraf GFETs are the only commercially scalable graphene devices that are manufactured using standard semiconductor processes and equipment, offering unparalleled quality and consistency. These research prototypes are produced by Paragraf's Foundry using patented technology and knowhow in 2D materials. Experiments were conducted with pristine graphene devices (flat, genuinely monolayer, free from polymer or metal contamination) pulled straight from stock to represent performance that can be achieved by any scientist without additional equipment. The experiments are performed with appropriate rigour and attention to detail, within a controlled experimental environment. They are not intended to mimic any particular product or application environment other than a laboratory.

The data shared herein is intended to serve as evidence of use case and exemplification that can be replicated independently. Further experimentation may build on these tests to establish specific product or application alternatives that meet specific needs or research interests.

Unmodified GFET-PV01 devices are on sale and in stock now via store.paragraf.com. Limited numbers of devices may be accessible as engineering prototypes on terms where performance data is shared. Please express your interest by emailing sales@paragraf.com.

Additional application notes are also available:

- pH sensing
- Potassium sensing
- Potassium sensing in serum samples

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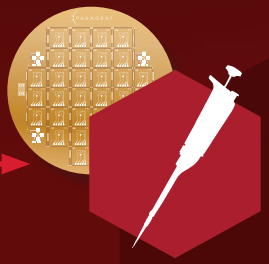
GFET-PV01 SPECIFICATION

EXPERIMENTAL METHODS AND RESULTS

GFET-PV01 devices were used for all experiments, at room temperature.

Pyrene Deposition

Pyrenebutyric acid (PyBA) was dissolved in anhydrous DMSO at 50 mM and lower concentration solutions made by serial dilutions.



GFET-PV01 devices were prepared by the Paragraf standard fabrication process. These devices were used without any further processing or conditioning of the surface.

Droplets of ca. 30 µL of PyBA DMSO solution were placed on the epoxy-enclosed cavity for two hours at room temperature.

All surfaces were then washed 3x with 30 µL DMSO, 3x with 30 µL ethanol then 3x with water, depositing the solvent onto the surface then aspirating each time.

Raman spectra were taken with a Horiba Scientific LabRAM HR Evolution equipped with a 11W 405 nm laser. Multiple measurements were taken across the sample with a 50x optic in a line, with each point being the result of the average of two measurements for five seconds. Optical checks were performed using a 20x optic to assess the state of the device and individual FETs.

Electrical results were then taken by connecting GFET-PV01 devices to 2x Keithley 2450 Source Measure Units with custom-built multiplexer device using an internal software. During this process, the charge neutrality point is initially established via a proprietary method, prior to a sweep transfer measurement taking place centred around the established charge neutrality point with a sweep width of 300 mV either side of this value.

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GFET-PV01 SPECIFICATION

Solvent compatibility

While numerous solvents have previously been used for the deposition of pyrenes onto graphene surfaces, the GFET-PV01's complex construction requires potential solvents to be tested for compatibility.

Solvent tests were performed by taking optical images of the exposed FET regions before and after a one-hour solvent exposure and observing the appearance of debris and markings on the surface. Such elements can be indicative of solvent incompatibility of one or more components. Only solvents previously shown to facilitate pyrene deposition were tested, with the addition of water for any aqueous media which the devices would be expected to be exposed to. An example comparison is shown in figure 1, showing the difference before (a) and after (b) solvent exposure to DMF.

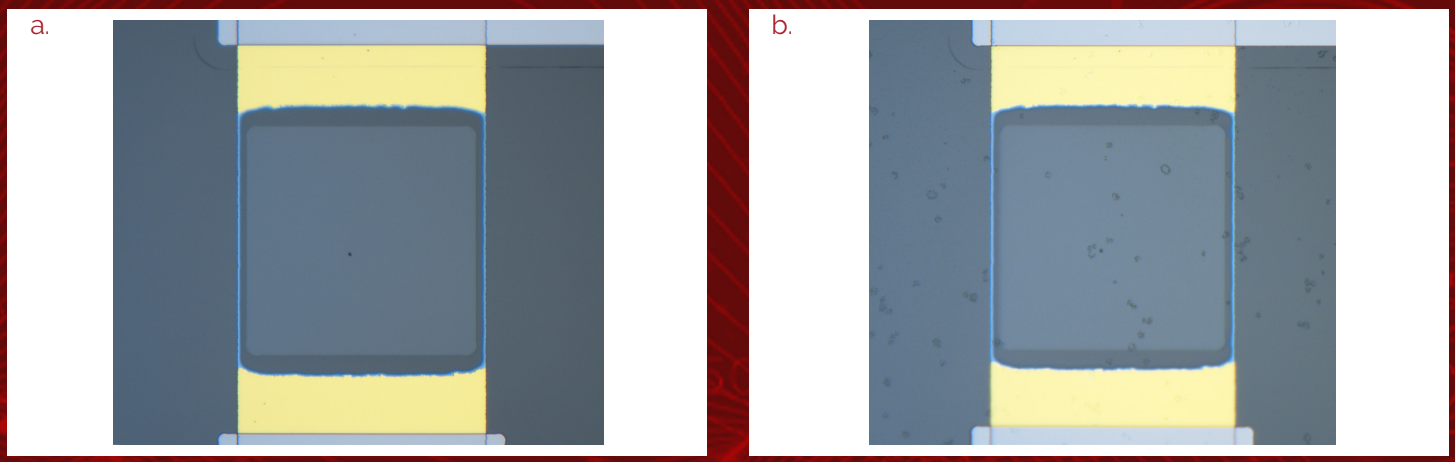

Figure 1.

a. FET region of the GFET-PV01 device prior to DMF exposure, with little to no debris present on the surface.

b. FET region of the GFET-PV01 device following DMF exposure, with clear debris visible on the surface, indicative of solvent incompatibility.

The following results were obtained via this method:

	Water	Dimethyl sulfoxide (DMSO)	Dimethylformamide (DMF)	Methanol	Ethanol
Compatibility	Good	Good	Bad	Fair	Good

From these results, DMSO showed the best compatibility with both the pyrene deposition and the solvent compatibility of the GFET-PV01 devices. As such all further experiments were performed in DMSO.

Results

As shown in Raman measurements, the incubation of any pyrenes resulted in the emergence of an additional peak in the 1127 – 1470 nm^{-1} region (herein called the pyrene peak), in addition to a shoulder at the higher side of the G peak.

In order to quantify the pyrene deposition, the ratio for the pyrene peak area/G peak area in Raman measurements was used as a measurement of the extent of the surface coverage with pyrene as shown in figure 2. Conducting these measurements at a range of pyrene concentrations led to the results shown in figure 3, with the negative control (DMSO only) shown in red. In addition to this, devices were also tested electrically to determine changes in the charge neutrality point as a result of the deposition. Example transfer curves are shown in figure 4, showing a clear shift upon pyrene incubation and combined results are presented in figure 5 showing a clear shift in charge neutrality point upon incubation with pyrenes in comparison to DMSO alone.

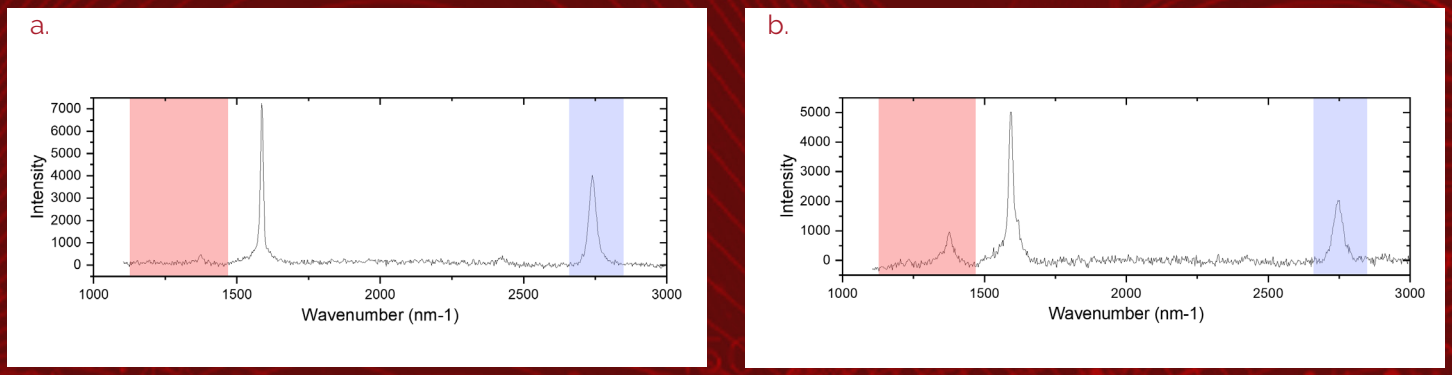

Figure 2.

a. Raman spectra of device surface following incubation with DMSO only (negative control) for two hours. The region for the pyrene peak (highlighted in red) and the 2D peak (highlighted in blue).

b. Raman spectra of device surface following incubation with 50 mM PyBA in DMSO for two hours. The emergence of both the pyrene peak and the high shoulder on the G peak indicates clear deposition of pyrenes on the surface.

Both spectra had a high background signal removed via fitting and removal of a polynomial function.

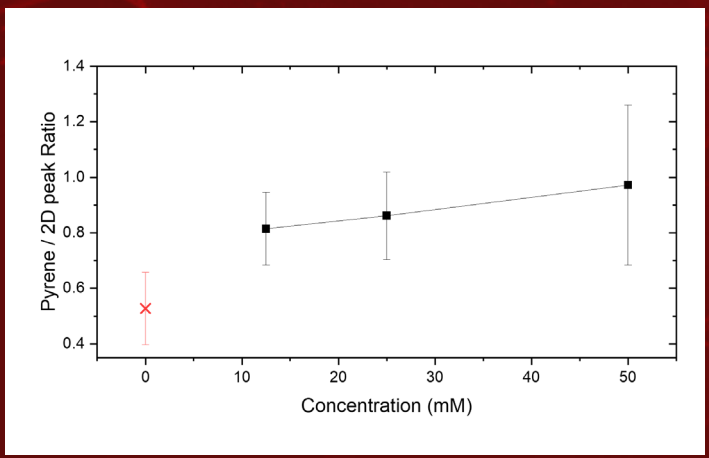

Figure 3.

Ratios of the peak areas from pyrene/2D in the spectra taken at multiple concentrations of PyBA. Negative control of DMSO only indicated by red cross.

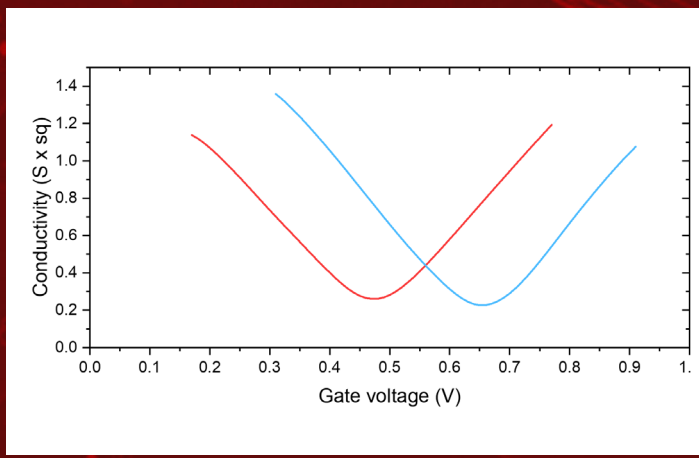

Figure 4.

Sweep transfer measurements for a device prior to (red) and following (blue) 25 mM PyBA deposition showing a clear large shift of the charge neutrality point of over 100mV to a more positive potential.

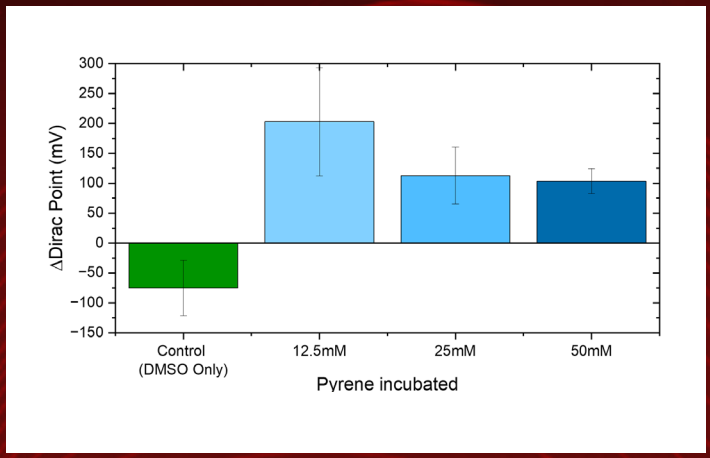

Figure 5.

Combined electrical shifts in the charge neutrality points for the pyrene incubations. Measurements taken from two devices x three FETs for each condition. Incubation with DMSO alone resulted in a negative shift in the charge neutrality point, while all concentrations of PyBA resulted in a positive shift.

It is proposed that the larger magnitude of the shift at the lowest concentration may actually be the result of a different conformation of the pyrene layer on the surface at this lower concentration as previous studies have suggested[1].

Recommendations

- The results presented here show a clear deposition of pyrenes on the surfaces of GFET-PV01 devices, confirmed by Raman spectroscopy and changes in the charge neutrality point.
- At this stage, we do not recommend the use of DMF or methanol solvents on the surface due to incompatibility with other components of the GFETo-PV01 device. Incubations with DMSO or aqueous solutions however have suitable compatibility.
- From the results presented, we would recommend use of 50 mM pyrenbutyric acid (PyBA) in DMSO incubated with the surface for two hours, followed by washes with DMSO, ethanol then water. This carboxylated surface then allows the use of EDC/NHS chemistry to generate an amine-reactive layer on the surface as an appealing target for further conjugation.

Reference

1. On Monolayer Formation of Pyrenebutyric Acid on Graphene
Malkolm Hinnemo, Jie Zhao, Patrik Ahlberg, Carl Hägglund, Viktor Djurberg, Ralph H. Scheicher, Shi-Li Zhang, and Zhi-Bin Zhang

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