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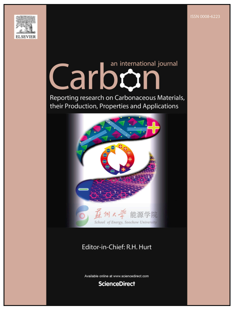

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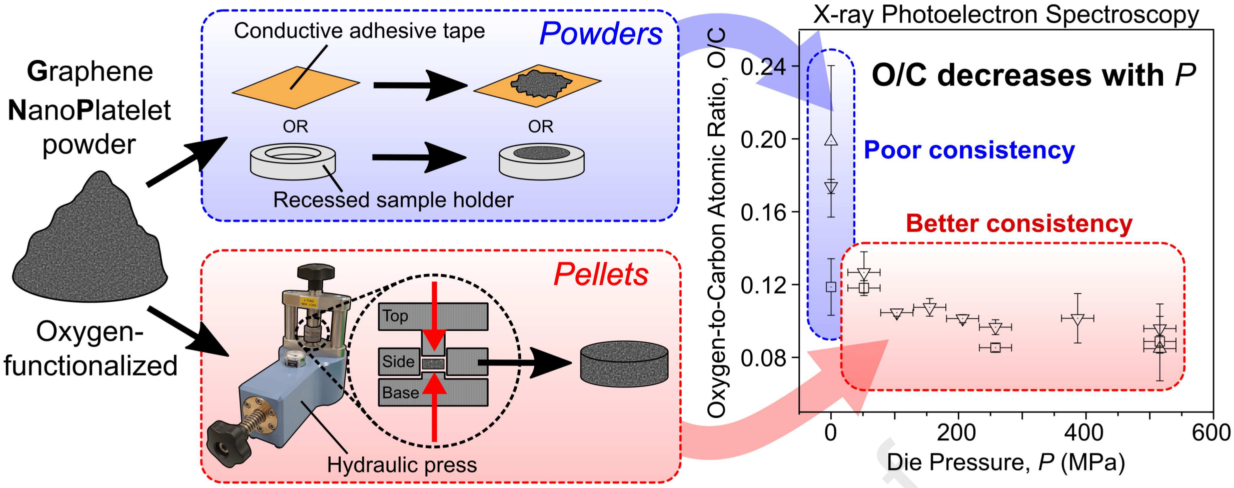
CREDIT AUTHOR STATEMENT

Benjamen Reed: Conceptualization, Methodology, Investigation, Formal analysis, Writing – Original Draft. **Sofia Marchesini:** Investigation, Formal analysis. **Giovanni Chemello:** Investigation, Formal analysis. **David J. Morgan:** Investigation, Formal analysis, Validation. **Neil Vyas:** Resources. **Thomas Howe:** Resources. **Jörg Radnik:** Resources, Writing - review & editing. **Charles A. Clifford:** Conceptualization, Supervision, Writing - review & editing. **Andrew J. Pollard:** Conceptualization, Supervision, Writing - review & editing


Graphene
NanoPlatelet
powder
Oxygen-
functionalized
Powders
Conductive adhesive tape
OR
OR
Recessed sample holder
Pellets
Top
Side
Base
Hydraulic press
X-ray Photoelectron Spectroscopy
O/C decreases with P
Poor consistency
Better consistency
Oxygen-to-Carbon Atomic Ratio, O/C
0.24
0.20
0.16
0.12
0.08
0
200
400
600
Die Pressure, P (MPa)

The influence of sample preparation on XPS quantification of oxygen-functionalised graphene nanoplatelets

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ABSTRACT

X-ray photoelectron spectroscopy (XPS) is widely used for characterising the chemistry of graphene-related two-dimensional materials (GR2M), however the careful preparation of the sample for analysis is important in obtaining representative quantifications. We report an investigation by three laboratories showing that the preparation method for oxygen-functionalised graphene nanoplatelet (GNP) powders has a significant effect on the homogeneous-equivalent elemental composition measured in XPS. We show that pressing GNP powders onto adhesive tapes, into recesses, or into solid pellets results in inconsistencies in the XPS quantification. The measured oxygen-to-carbon atomic ratio from GNP pellets depends upon the die pressure used to form them and the morphology of the GNPs themselves. We recommend that powder samples of GR2Ms are pelletised prior to XPS analysis to improve repeatability and reproducibility of measurements.

1. INTRODUCTION

Graphene continues to attract significant interest from academia and industry with its remarkable properties, such as high room-temperature electron mobility,[1] thermal conductivity,[2] mechanical strength,[3] nonlinear optical properties,[4] and its exceptionally high specific surface area.[5] In particular, there are many small-to-medium enterprises that aim to commercialise the material for a multitude of applications ranging from electronics and optoelectronics,[6] detection and sensing devices,[7,8] biosystems,[9] through to chemical and environmental corrosion inhibition.[10]

Currently, graphene nanoplatelets (GNPs) can be produced in large quantities using various bottom-up and top-down methods.[11] However, the material properties of industrially produced powders containing graphene related 2D materials (GR2Ms), particularly functionalised and unfunctionalised GNPs, can vary considerably depending on the production method.[12] In particular, the surface chemistry, modified through chemical functionalisation processes, can significantly affect dispersibility of particles in solvents and matrixes, which is important for embedding GNPs into real-world products. For example, to produce nanocomposites, the surface functional groups present on GNPs must be optimised to bond with the matrix and improve mechanical properties in the resulting composite.[13]

To accelerate the adoption of graphene, the industry needs reliable methods to measure the surface chemistry of GNPs, to standardise quantification of this material property, allowing industry across the supply chain to compare different commercially supplied GNP powders.[14,15] X-ray photoelectron spectroscopy (XPS) is a reliable quantitative technique for determining the elemental and chemical composition of materials.[16] It is therefore widely used, and misused,[17] for the chemical characterisation of GNPs. XPS is a highly surface sensitive technique, with electron effective attenuation lengths of typically 2 nm to 3 nm. This surface sensitivity makes analysis and data interpretation susceptible to complications from surface contamination. Contamination arises from sample storage, handling, and exposure to ambient conditions. Careful sample handling and preparation methods are required to protect the region of interest, as shown by Stevie *et al.*[18] Powders in particular require care because loose particles can cause damage to an XPS instrument if they reach the lens column of the analyser or the blades of a turbomolecular pump. Common methods for immobilising powder samples include: spreading over adhesive tape; lightly tamping into a small recess; dispersion and deposition using an appropriate solvent; pressing into a soft metal such as indium; and pressing into a pellet of material using a pellet press. GR2Ms are no exception and require careful preparation before an XPS measurement.

An ISO documentary standard (ISO/TS 23359) is currently under development within ISO/TC 229 (Nanotechnologies) that addresses the chemical characterisation of GR2Ms in powders and liquid dispersions using primarily XPS along with three other optional techniques.[19]

International measurement standards require robust metrological investigations to determine the size and source of variance affecting the results, in this case from sample preparation for powders containing GNPs. This work will contribute to this effort by assessing the sample preparation of GNPs for XPS analysis.

In this paper, we provide evidence that the measured elemental composition of GNPs in a powder form is dependent upon the sample preparation technique used, specifically for the case of immobilisation of powders into solid pellets. Using data from three laboratories denoted as A, B, and C, we demonstrate that the preparation method of oxygen-functionalised GNP powders can have a measurable effect on the homogeneous-equivalent elemental composition measured by XPS. We show that the variance of the interlaboratory measurements on GNP powder samples is greater when compared to pellets of the same materials. We show that the application of pressure to press these powders into adhesive tape or form into solid pellets will give different results in XPS quantification. The results depend upon the pressure used and the morphology of the GNPs themselves. Inconsistent sample preparation poses a significant reproducibility challenge for industries that rely on consistent quantification of their GR2Ms using XPS. We also provide a recommendation for best practice when preparing samples of powders containing GR2Ms for analysis by XPS.

2. METHODS

Commercial graphene powders, both raw and functionalised, were provided by Haydale Ltd. (Ammanford, U.K.). The starting material consisted of two different types of commercially produced nominal few-layer graphene powder. These were chosen to have differing morphologies and named here G5 and G6. G5 was chosen to have larger particles and was produced commercially using a top-down process whereas G6 consisted of smaller non-planar particles and was produced from a commercial bottom-up process. The G5 and G6 powders were analysed as powders and pellets. In addition, the same starting materials were Oxygen-functionalised (O) by Haydale Ltd. using a plasma treatment where the G5 and G6 powders were placed separately into a patented reactor barrel and loaded into a HDPlas® plasma reactor. High nitrogen-content feed gas was fed into a low-pressure chamber where it was energized and ionized to create a plasma. Gas flow and pressure were regulated by a mass flow controller and a metered vacuum source. The reactor barrel both acted as a counter-electrode and rotated around the central electrode to facilitate mixing. The reaction process integrated pre-treatment and post-treatment to ensure homogeneity of the starting material and product.

Samples of the four powders were prepared in two forms for XPS measurements, shown schematically in Figure 1(a). Samples were prepared separately by each laboratory to avoid comprising the integrity of samples due to vibrations because of transportation. Sample preparation was conducted in laboratories with temperatures between 19℃ and 21℃, and relative humidity between 35 % and 45 %. The first method aimed to immobilise the powders by either using adhesive tape or a recessed sample holder. These are identified as “powder” samples because they rely on manual low force pressing or manipulation of the GNP samples which is unlikely to be consistent across samples. To immobilise with tape, a small piece (~0.5 cm × 0.5 cm) of conductive adhesive tape was attached to the XPS sample plate (N.B. Carbon tape was specifically not used to avoid erroneously measuring the carbon particles in the tape). Then a small quantity of powder was scooped onto the tape using a spoon spatula and pressed using the flat end. Care was taken to ensure a uniform coverage of powder on the adhesive with no cracks or voids. The sample holder was then tilted and firmly tapped to remove any loose powder. If any gaps in the powder were observed, then additional powder was pressed into these areas to ensure total coverage. Alternatively, a small quantity of powder was deposited into a recessed sample holder and then lightly pressed flat using a UV-ozone cleaned glass slide. In the second method, a small quantity of powder was mechanically pressed in a small hydraulic press (Specac Ltd, Orpington, UK) by applying a force onto a (7.0 ± 0.1) mm diameter, round, pellet die, therefore producing a solid pellet. These are identified as “pellet” samples. Prior to preparing pellet samples, each die surface was inspected for any obvious damage or deformation. They were then cleaned by sonicating the opposing die surfaces separately in isopropanol alcohol (IPA) for at least 10 minutes, and then wiping the die surfaces with a lint-free IPA-soaked cloth. Between successive pellet pressings, the die was cleaned again using the same method.

After sample preparation, laboratories A and B had the following powder ($_{\text{PW}}$) and pellet ($_{\text{PT}}$) samples: G5$_{\text{PT}}$, G5-O$_{\text{PT}}$, G6$_{\text{PT}}$, G6-O$_{\text{PT}}$, G5$_{\text{PW}}$, G5-O$_{\text{PW}}$, G6$_{\text{PW}}$, G6-O$_{\text{PW}}$ (8 samples in total). The pellets were made using an indicated load of (2.00 ± 0.05) long tons, which corresponds to a pressure in international standard units of (518 ± 25) MPa, ensuring that the pellets stayed solid throughout sample mounting and measurements. In addition, pellets of G5-O and G6-O were produced at lower pressures to investigate the effect of pellet formation pressure on the measured elemental composition. Laboratory C produced G6-O pellets using pressures of 52 MPa, 104 MPa, 155 MPa, 207 MPa, 259 MPa, 388 MPa, and 518 MPa. Laboratory A produced G5-O pellets using pressures at 52 MPa and 259 MPa. The pellet formation pressure uncertainty was 25 MPa in all cases.

XPS measurements were conducted by each of the three laboratories involved in the study. Laboratories A and B used an AXIS Ultra DLD (Kratos Analytical Ltd, U.K.) and laboratory C used a K-Alpha$^+$ (Thermo Scientific Inc., U.K.). All XPS instruments used in this study had base pressures less than 5.0×10^{-9} mbar. Individual system base pressures are stated in the supporting information (SI). Each laboratory used their own standard protocols for instrument calibration, data acquisition, and analysis, which are detailed in the SI. All instruments used in this study were energy and intensity calibrated. The selection of analysis locations for XPS was consistent for both powder and pellet samples, avoiding obvious topographical features where possible, for example: cracks, flakes, and ridges. All spectra were acquired at an emission angle of 0° (take-off angle of 90°). Complementary measurements were conducted by laboratory A using nitrogen gas physisorption and laboratory B using scanning electron microscopy (SEM). Nitrogen physisorption measurements were obtained using an ASAP 2460 (Micromeritics Ltd, U.K.) sorption analyser and analysed using the Brunauer–Emmett–Teller (BET) equation to measure the surface area from nitrogen sorption isotherms. SEM images were obtained using a SUPRA 40 (Carl Zeiss AG, Germany), with a Schottky field emitter and a secondary electron InLens detector, to obtain high-resolution images. Further details on each method are included in the SI.

3. RESULTS AND DISCUSSION

Figure 1(b) shows the C 1s and O 1s core level peaks from representative survey spectra of G5-O and G6-O as pellets and powders. The C1s peak is observed at 284.3 eV, consistent with carbon in the sp^2 hybridisation state, and there is also a feature at ~291 eV which is the typical position of the π- π^* transition of graphitic carbon. The O 1s is observed at 532 eV which is consistent with carbon bonded to oxygen. These spectra have been normalised to the maximum signal of the C 1s peak to show the differences in the intensity of the O 1s peak between different samples and instruments. The full energy range of the spectra shown in Figure 1(b) are provided in Figure S1 in the SI. Representative high-resolution C 1s and O 1s spectra for G5-O and G6-O are shown in Figure S2, both in the SI. The C 1s high resolution spectra have also been peak fitted using the model from Marchesini *et al.* to determine the carbon-oxygen chemical environment, which is also shown in Figure S2 in the SI. [20–22]

The results in Figure 1 show differences in the atomic composition between the raw and O-functionalised materials depending on their sample preparation for XPS analysis. The G6-O material exhibits an increased O 1s intensity compared to the G5-O material. There are also subtle differences in the O 1s intensity between the powder and pellets samples of both materials, although the lack of change in the peak lineshape and energy positions indicate that the chemical environment of oxygen remains consistent. Figure 1(c) shows the homogeneous equivalent atomic composition [23] measured on all samples ($G5_{PT}$, $G5\text{-}O_{PT}$, $G6_{PT}$, $G6\text{-}O_{PT}$, $G5_{PW}$, $G5\text{-}O_{PW}$, $G6_{PW}$, $G6\text{-}O_{PW}$) by each laboratory. Quantification results extracted from the survey spectra (also called wide scans) are shown in Table S2 in the SI. Figure 1(d) demonstrates the percentage change in the measured atomic fraction of oxygen ([O]) between the pelletised ($[O]_{Pellet}$) and powder materials ($[O]_{Powder}$). The blue bars correspond to laboratory A's measurements, the pink bars to laboratory B's measurements, and the orange bars to laboratory C's measurements. The y-axis is equal to $[O]_{Pellet} - [O]_{Powder}$, therefore a positive at.% value indicates that the [O] of a pellet sample is greater than the powder sample of the same material, measured at the same laboratory. Figures 1(c) and 1(d) present two sources of inconsistency in the atomic composition quantification of these graphitic particles. The sample-to-sample variability (i.e. the intra-laboratory variability) is shown in Figure S3, and is below 5 % for both the pellet and the powder samples.

The first inconsistency is that, in some cases, the laboratories measure different values of [O] for the same material *and* preparation. In Figure 1(c) for example, there is a 1.5 at.% difference between the laboratories in the measurement of [O] for both $G5\text{-}O_{PW}$ and $G6_{PW}$, and a 1.1 at.% difference for $G6_{PT}$. Smaller differences of less than 0.4 at.% are observed for $G5_{PW}$, $G5_{PT}$, $G5\text{-}O_{PT}$, and $G6\text{-}O_{PT}$. The largest inconsistency is observed for $G6\text{-}O_{PW}$, which exhibits a 6.0 at.% difference between laboratories A and B. It is useful to present these atomic fraction differences between laboratories as a *relative percent difference*, $\Delta_{[O]}$. This is defined as the absolute difference in maximum and minimum [O] measured between all laboratories, i.e. the range $[O]_{Max} - [O]_{Min}$, divided by the average value of [O] from all laboratories, i.e. $[O]_{Mean}$. This is mathematically shown in Eqn [1] as:

$$\Delta_{[O]} = 100 \times \left| \frac{[O]_{Max} - [O]_{Min}}{[O]_{Mean}} \right| \qquad \text{Eqn [1]}$$

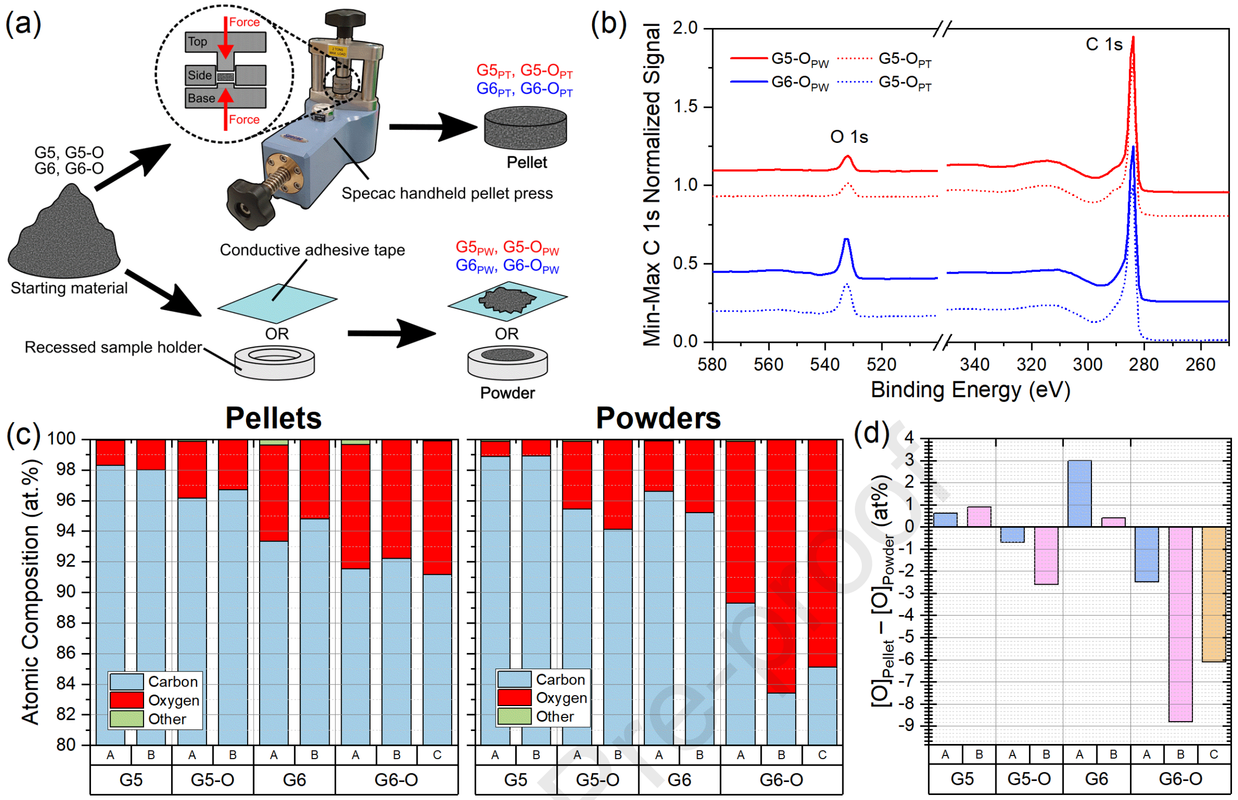

Figure 1. Interlaboratory comparison of elemental composition of oxygen-functionalised graphene. (a) A simplified procedure schematic showing the preparation of the starting material into solid pellets and immobilised powder specimens. **(b)** O 1s and C 1s core levels from representative survey spectra of G5-O (PT and PW) and G6-O (PT and PW) acquired by laboratory A. **(c)** Elemental composition comparison between laboratory A and B for the same materials after preparation as a pellet or a powder, and G6-O powder sample from laboratory C. The origin of the 'Other' observed elements is discussed in the SI. **(d)** A bar chart showing the difference in oxygen atomic fraction between pellet and powder preparation for each material and measurement laboratory.

The $\Delta_{[O]}$ values of the pellet samples range from ~11 % to ~22 %, with an average $\Delta_{[O]}$ of ~16 %. This is within the calculated combined uncertainty of sensitivity factors,[24] background selection,[23] and intensity relative response function.[25] This interlaboratory variation is generally reduced by following consistent protocols for XPS measurement and data analysis, such as the ISO standards on photoelectron spectroscopies (developed by ISO/TC 201/SC 7).[26] There are ongoing efforts by XPS experts to address reproducibility issues through interlaboratory studies like this and the provision of guidance publications.[27] Whilst it is common practice to extract atomic composition from survey spectra, it is also possible to use the high-resolution scans for the same purpose and, in fact, it is advised when the atomic fraction is very low or near trace amounts (i.e. < 1 at.%).[24] For this study, a comparison of atomic composition extracted from survey spectra and high-resolution narrow scans is shown in Table

S3 in the SI. This comparison demonstrates that the same results are obtained by either quantification method within an average relative percentage difference (defined by Equation S1 in the SI) of ~5 % (over a range of ~1 % to ~10 %), which is again within the expected combined uncertainty. [23–25]

In comparison, the $\Delta_{[O]}$ values of the powder samples range from ~11 % to ~43 %, with an average $\Delta_{[O]}$ of ~30 %. Whilst the observed relative percentage differences between labs for both powders and pellets are expected for low oxygen concentrations, there is an observable two-fold increase in variation in the powder measurements (~30 %) compared to the pellet measurements (~14 %). This additional interlaboratory variation in the powder measurements is likely due to differences in each laboratory's powder preparation method. Laboratory A and B used adhesive tape to immobilise the powders, whereas laboratory C used a powder recess. The amount of pressure applied to the powders to 'flatten' or 'tamp' them could not be measured and depends upon the analyst, in contrast to pelletisation which applies a known force across a known area. Sample roughness is also a factor that cannot be avoided and likely contributes to differences in the atomic composition over a sample surface. For example, the use of tools such as spatulas or tweezers to smooth powder samples may introduce roughening. For pellet samples, not cleaning the pellet die between multiple pelletisation attempts also caused significant visible roughness on the pellet surfaces, resulting in increased variation in the atomic composition measurement, as shown by Figure S4 in the SI.

The second inconsistency is the absolute difference in [O] between material prepared as powders and those formed into pellets. Figure 1(d) shows that the unfunctionalised materials exhibit a small increase in [O] after pelletising in both laboratories which is likely due to contamination from the die. In contrast, oxygen-functionalised materials show a large decrease in the [O] after pelletising. These differences in the [O] between powders and pellets signal a potential reproducibility issue, so further investigation into the effect of pelletisation on GR2Ms was carried out. Figure 2 shows the oxygen-to-carbon atomic ratios (i.e. [O]/[C], herein shown as O/C) of the oxygen functionalised particles with increasing pellet formation pressure where data from all three laboratories has been included. In both Figures 2(a) and (b), the zero-pressure mark denotes a powder measurement (i.e. powder deposited on adhesive tape or into a recess). The full quantification results are shown in Table S4 in the SI. Each data point represents the mean O/C measured by that laboratory for that pressure. The y-error bars indicating the expanded uncertainty, U, as three times the standard deviation, σ (i.e. $U = \pm 3\sigma$) of the individual O/C measurements (except for laboratory B data, see Table S5). The x-error bars indicate the combined uncertainty of the analogue dial measurement of the pellet press and the dimensions of the die (See Table S5 for error analysis). For both G5-O and G6-O material, increasing the pellet formation pressure causes a decrease in the measured O/C, as shown by Figure 2(a) and Figure 2(b) respectively. This observation is consistent with the data shown in Figure 1. There is a major decrease in the O/C for both samples from the powder to the first pellet formation pressure of 52 MPa. After this initial application of pressure, both materials appear to show smaller decreases of O/C with increasing pressure.

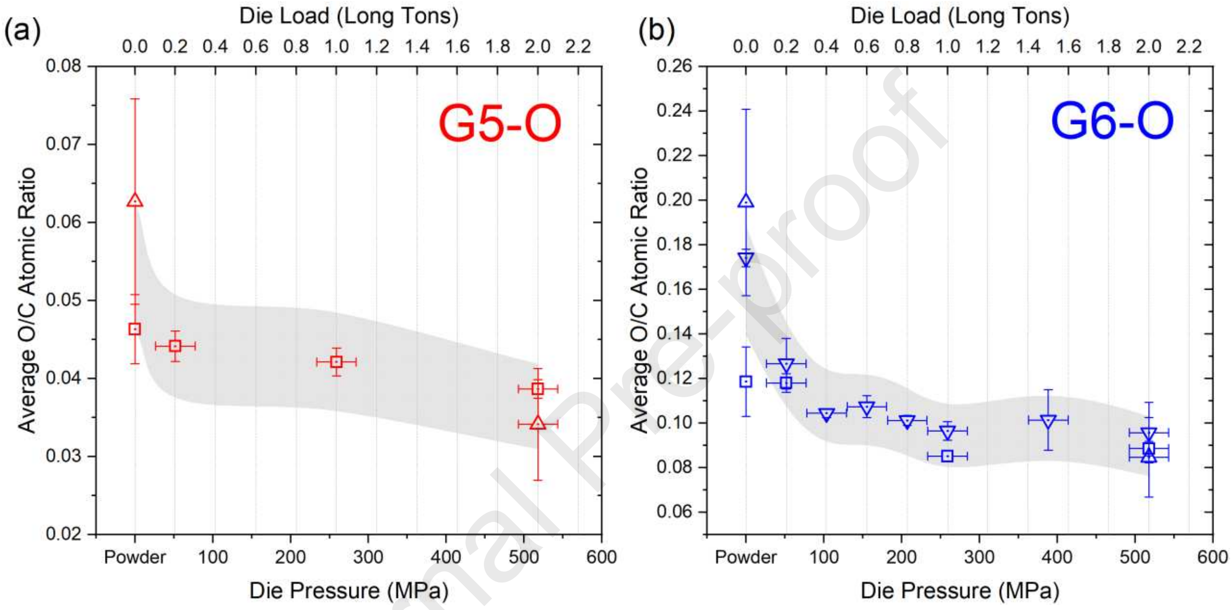

Figure 2. Influence of pellet formation pressure on elemental quantification of oxygen functionalised graphene. Square data points were from laboratory A, triangle data points from laboratory B, and inverted triangle data points from laboratory C. **(a)** O/C of G5-O with increasing pellet formation pressure. **(b)** O/C of G6-O with increasing pellet formation pressure. In both materials, the application of pressure to form pellet alters the measured oxygen content of the sample resulting in reduced O/C in quantification. In both graphs, the grey shaded region shows the calculated combined uncertainty of sensitivity factors,[24] background selection,[23] and the intensity relative response function.[25]

It is likely that the O/C ratio response to pressure depends upon powder morphology. Figure 3 shows SEM images acquired from the unfunctionalised material before and after pelletisation. There is a clear difference in morphology between the two materials. Figures 3(a) shows an SEM image acquired from G5$_{PW}$, which is has large, planar particles up to ~100 µm in their largest dimension. Figure 3(b) shows an SEM image acquired from G6$_{PW}$, which has comparatively smaller, non-planar particles with a largest dimension typically ~100 nm, with larger agglomerates of ~500 nm. Images acquired at higher magnification are shown in Figure S3 in the SI. Moreover, a change in morphology is also observed within the same samples after pelletisation (Figure 3(c) and Figure 3(d)), showing a smoother surface with apparent reduction in macroscale roughness for both samples. There is also some initial evidence that particle orientation influences the measured O/C ratio. When a G5-O_{PT} is cut in half (to reveal the 'bulk' structure) parallel to the pellet surface, the measured O/C of the exposed surface is equal to the pellet surface (within increased variance due to roughening). However there is an observable increase in the O/C on the exposed surface of the pellet cut in half perpendicular to the pellet surface. In the case of G5-O, the GNP particles are large and have a planar structure and oxygen functionalisation can occur on the platelet edges.[28] One hypothesis is that in a sample of randomly orientated oxygen functionalised GNP particles, for example as in a powder sample, some fraction of particles at the surface will have their oxygen functionalised edges pointing up toward the XPS instrument's lens column. This effectively acts like an oxygen enriched layer (or overlayer) at the surface of the sample, leading to an increase in the oxygen content measured in the XPS spectrum. Pelletisation may force these planar particles to lie flat during compaction of the powder to a pellet, resulting in a more homogeneous chemically distributed surface and a lower measured oxygen content. There is still further investigation required to test this hypothesis, but initial evidence, from both the SEM in Figure 3(a–d) and the XPS in Figure S6, seems to suggest that a physical mechanism is responsible for the observed changes in O/C. This is further supported by the lack of change in the chemical environment between pellet and powder samples, as shown in Figure S2 in the SI.

Nitrogen sorption isotherms at 77 K were also collected for powder and pellet samples to monitor changes in textural properties of materials such as pore volume and specific surface areas (SSAs) and are shown in Figure 3(e). BET SSAs of each material were calculated and are shown in Table S6 in the SI. Nitrogen sorption isotherms show a significant difference between the G5 and G6 samples. The isotherm shape for G5 resembles that of a non-porous or macroporous material, with small uptakes at low relative pressure and relatively low BET SSA.[29] G6 samples showed a higher uptake at low relative pressures, indicating the presence of micropores (pores with diameter less than 2 nm) and the presence of a hysteresis in the desorption curve, indicating the presence of mesopores (pores with diameter between 2 and 50 nm).[29] The shape of the hysteresis suggests the presence of slit-shape pores,[29] as expected for 2D materials. For both samples, pelletisation caused a reduction in the total nitrogen uptake in the high-pressure region as shown in the lower panels of Figure 3(e), which is indicative of reduction in total pore volume. Small reductions of BET SSA were measured (Table S6 in the SI) as well as minor changes observed in the lower pressure region, indicating small reduction to the micropore volume.[29]

The small changes in SSA after pelletisation indicate that graphitic particles did not fully re-stack and/or smaller pores didn't fully disappear.

These results demonstrate that there is necessity for harmonised operating procedures for GNP sample preparation (and GR2Ms in general) for surface analysis measurements such as XPS, to allow comparison of materials measured by different laboratories or at different stages of their life cycle. Based on the results of this limited interlaboratory study, the recommendation is that GR2Ms should be pelletised before XPS analysis. We also recommend where possible, that a dedicated die should be used for GR2Ms to prevent transfer and contamination of non-GR2Ms during pelletisation. Analysts should also consider the scratch hardness of their pellet die and ensure that hard materials do not damage or deform the die surfaces and increase the likelihood of contamination. Participating laboratories in this study had access to the same pelletisation apparatus, which is not a guarantee for every laboratory preparing GR2Ms. Therefore, reporting the pellet formation pressure value in the international system of units permits the comparison of results from different laboratories. Selecting a standard pellet formation pressure is not trivial, because different GNPs may or may not form a solid pellet readily depending on their morphology. It should be noted that whilst the method of pellet sample preparation discussed here is known to work for GR2Ms, it may be unsuitable for other material systems. Therefore, further studies are required to identify suitable procedures and best practice that can be implemented across a broad range of materials to enable comparability. In any case, there must be detailed reporting of the sample preparation procedure, especially when measuring GR2M powders, to allow any meaningful comparison between different experiments and laboratories.

As of writing, there is an international interlaboratory study being conducted under the auspices of technical working area 2 of the VAMAS (Versailles Project on Advanced Materials and Standards) organisation which aims to validate methods for chemical characterisation of functionalised graphene nanoplatelets using XPS and determine the uncertainties associated with the measurements and data analysis.

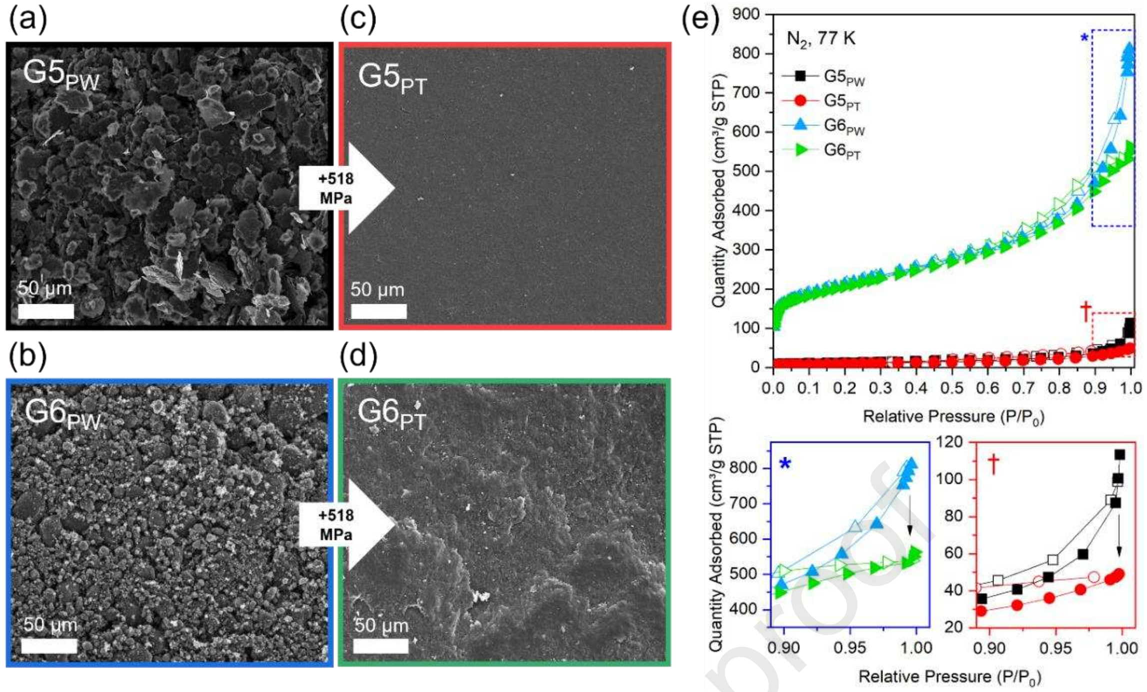

Figure 3. Textural properties of unfunctionalised G5 and G6 materials. (a-b) SEM images of G5 and G6 powders samples respectively; **(c-d)** SEM image of G5 and G6 pellet samples respectively, formed using a die pressure of (518 ± 25) MPa; **(e)** N_2 physisorption isotherms collected at 77 K for powder and pellet materials as well as insets showing the high-pressure regions of the G6 samples (blue star) and the G5 samples (red dagger).

4. CONCLUSIONS

Inconsistent sample preparation poses a significant reproducibility challenge for industries that rely on consistent quantification of their GR2Ms using XPS. In this work, we demonstrated that the method of sample preparation for GNPs has a measurable effect on both the interlaboratory variability *and* the homogeneous equivalent atomic composition measured by XPS. The relative percentage difference in [O] between laboratories is greater for powder samples (30 %) compared to pelletised samples (16 %) which is attributed to differences in sample preparation techniques which may affect surface roughening or cause surface contamination. Pelletisation results in a different measured homogeneous equivalent atomic composition for GNPs. In general, we find that there is a significant difference in the O/C atomic ratio from powders to pellets for the same material, approximately on the order of 44 %. There is also a continued but less pronounced decrease in the O/C for oxygen functionalised material with increasing pellet formation pressure, which preliminary evidence suggests may be due to a physical mechanism of nanoplatelet orientation. Complementary SEM and BET measurements confirm that structural changes occur between powder and pellet samples in conjunction with changes in the atomic composition.

Pelletisation is therefore the preferred sample preparation method for GNPs (and GR2Ms in general) because it demonstrates improved repeatability and reproducibility by reduced variation in quantification from different analysis areas and different laboratories. The die pressure used to form pellets should be reported, and it is also important to report the morphology and structural properties of GR2Ms, for example SEM and BET data, to support the XPS results.

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AUTHOR CONTRIBUTION STATEMENT

Benjamen Reed: Conceptualization, Methodology, Investigation, Formal analysis, Writing – Original Draft. **Sofia Marchesini:** Investigation, Formal analysis. **Giovanni Chemello:** Investigation, Formal analysis. **David J. Morgan:** Investigation, Formal analysis, Validation. **Neil Vyas:** Resources. **Thomas Howe:** Resources. **Jörg Radnik:** Resources, Writing - review & editing. **Charles A. Clifford:** Conceptualization, Supervision, Writing - review & editing. **Andrew J. Pollard:** Conceptualization, Supervision, Writing - review & editing

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: