

Interactional fingerprints offer an accessible, rapid, means to characterise graphene oxide.

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ABSTRACT

Graphene-based materials (GBMs), including graphene oxide and graphene, are atomically thin materials with great promise, but efforts to realise this promise have been hampered by inconsistent material supply and the lack of rapid, accessible, characterisation methods. Here we present a new approach, based on surface interaction with a series of probe molecules, to rapidly provide a qualitative characterisation of graphene oxide materials at low cost, using widely available instruments. We demonstrate that our method can make qualitative comparisons, allowing us to observe if batches of material differ. Furthermore, in some circumstances it can quantify systematic differences, such as surface modification. We propose this approach may prove a valuable quality control method for materials producers and users alike and, since many applications of graphene oxide — and 2D materials in general — depend on surface interactions, and suggest this kind characterisation may be valuable beyond rapid QC, in GBMs and other materials.

Keywords: graphene oxide, supramolecular chemistry, sensor array, interactional fingerprint, quality control, material characterisation.

INTRODUCTION

Graphene, graphene oxide, and other "graphene-based materials" (GBMs) are materials based on a single layer of carbon, only one atom thick.^{1,2} Following the isolation of graphene in the early 21st Century^{3,4} they have been hailed as 'wonder materials', and vast sums have been invested in developing applications.⁵ This promise is real: atomically-thin, and 'few-layer', flakes of material have very distinct, and exciting electronic and mechanical properties (c.f. 'bulk' materials), with potential applications in electronics, clean energy, and sensor applications.⁶ Over fifteen years later, though, much of this promise has not yet been realised.⁵ Anecdotally, it has been known for some time that a barrier to adoption of GBMs has been unreliable supply of materials, leading to irreproducible results: users complain that using the "same" material, purchased from the same supplier, can produce distinct results. A recent study surveying commercially-available graphene materials brought the extent of the problem to light: the majority of samples analysed contained less than 10% single layer graphene, with authors summing up that "*producers are labeling black*

powders as graphene and selling for top dollar, while in reality they contain mostly cheap graphite".⁷ A 2023 study of graphene oxide similarly found only a small fraction "*deliver approximately what they display on the label or brochure*". The authors of those studies, and widespread comment,^{8,9} suggest that this issue represents a barrier to realising GBMs' potential, and suggest quality control and characterisation by both producers and users of material as the remedy.

Until recently, there has been little agreement on what constitutes appropriate characterisation. This has been partially addressed by the publication of an International Standard for graphene characterisation in 2021.^{10,11} This approach involved rigorous characterisation involving a range of instrumental procedures, including Raman spectroscopy, electron microscopy (either Scanning Electronic Microscopy, SEM, or Transmission Electron Microscopy, TEM), Atomic Force Microscopy (AFM), and measurement of surface area using gas physisorption (by the Brunauer–Emmett–Teller method, BET). While no corresponding International Standard has yet been

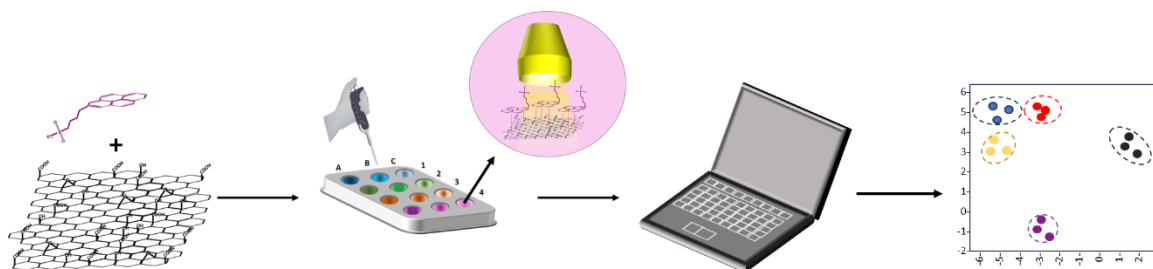


Figure 1. Concept and workflow for rapid interactional fingerprinting assay. In each well of an appropriate microplate, each of a series of probe molecules is mixed with a GO dispersion sample; where probes interact with the GO surface, a change in the probes' fluorescence can be observed; this series of responses can be considered an 'interactional fingerprint'. Deconvoluting this fingerprint data for a series of GO samples (e.g. by Principal Component Analysis, PCA, or Linear Discriminant Analysis, LDA) can provide a readout or 'map', showing whether samples differ.

published for graphene oxide, which has more complex surface chemistry, an analogous 'gold standard' approach would include the same, with the addition of X-Ray Photoelectron Spectroscopy, to determine the abundance of carboxylic acid, alcohol, and epoxide groups (demonstrated in a recent survey of supply).¹² Such characterisation is desirable, but is typically slow, costly, inaccessible, and requires specialised personnel, making it inaccessible to many labs (both academic and industrial).

More accessible characterisation methods are clearly needed: for materials producers and users alike to perform quality control (QC) testing. Such methods should be rapid (hours, not weeks), cheap (few dollars, not thousands of dollars), use only widely available apparatus, and be feasibly performed by technical staff in a non-specialist lab setting or factory. Importantly, routine methods need not provide the same level of structural and chemical insight as 'gold standard' methods: the ability to compare materials, and identify changes – that is, to allow the user to ask "Is this material like other batches?" – is sufficient for many QC needs.¹¹ Some materials users opt to apply a subset of gold standard techniques, sometimes combined with other methods such as Dynamic Light Scattering (DLS),¹³ pKa measurement,¹⁴ NMR relaxation,¹⁵ and covalent attachment of dyes to quantify surface functional groups,¹⁶ but most of these do not fulfil material users' needs for a rapid, cheap, accessible method covering a range of properties, and have not been widely adopted.

This work focusses on the rapid characterisation of GO, since it is a particularly challenging GBM, produced by a range of manufacturing methods which yield wide variation of its surface chemistry,^{12,17} and with many applications which depend on the effect that this has on surfaces' molecular recognition and aggregation properties.^{18,19}

Here we demonstrate a new approach to QC testing for graphene oxide (GO), based on the interaction of an array of probe molecules with GO surfaces, as outlined in Figure 1. The approach is similar to other supramolecular sensor/probe arrays with optical detection:^{20–22} when molecular probes interact with aqueous GBM dispersions, their signal (absorbance or fluorescence) is quenched, providing a ready, rapid, means to measure interaction. One probe molecule's interaction cannot characterise the many variables describing a material. However, if a series (or "array") of different probes interact with distinct sites, with distinct affinities, the distribution of responses constitutes an 'interactional fingerprint' incorporating information on many variables (see Figure 3A). Deconvolution of fingerprints by multivariate analysis methods provides readout of sample composition: for our purposes, this is usually regression process, producing a 2D map, where adjacent materials are similar. A small range of GBM characterisation methods based on non-covalent interactions have already been reported. These include adsorption for surface area measurement (using gases,²³ methylene blue dye²⁴ and/or dopamine),²⁵ and fluorescence quenching for optical microscopy.²⁶ These are limited, only

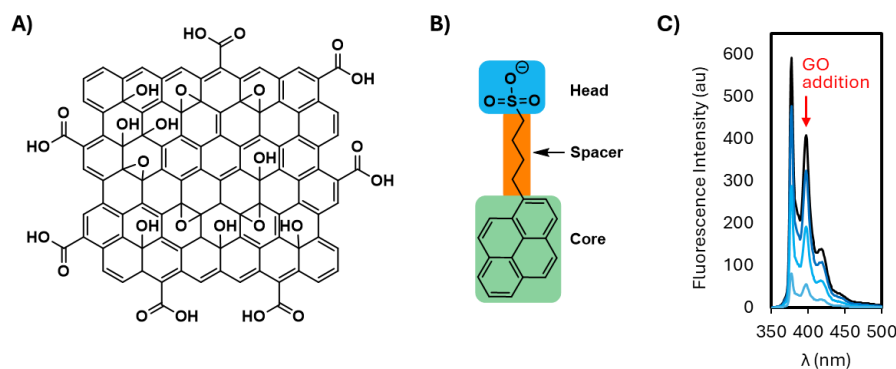


Figure 2. Establishing probe quenching on interaction with GO. A suitable probe for a GO surface (A) should incorporate moieties shown in (B), and its fluorescence must be quenched on interaction with GO surfaces (C, quenching of P1 on addition of GO).

providing information on one variable (size), and this may only apply in the unlikely event that other variables do not change; so far few authors (or industry contacts) report their routine use. A paper on electrochemical study of phenols' surface interactions at GO surfaces suggests this may be used to understand GO composition,²⁷ but we find no citing work following this suggestion. This work provides an alternative approach.

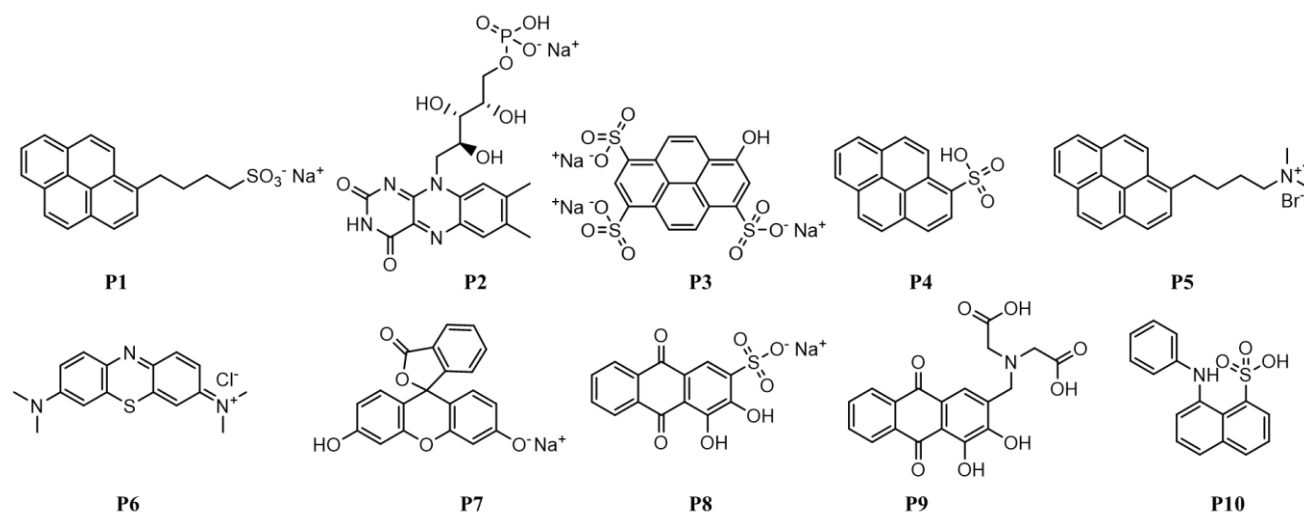
RESULTS

Establishing a Probe Array

To construct a probe/sensor array, we require probe molecules which, (i) interact with the analyte, GO surfaces, and (ii) provide a measurable signal change when they interact. Fluorescent probes are well-suited, as interaction with GO typically quenches fluorescence via an energy transfer mechanism,²⁸ and the means to measure this change (fluorescence microplate readers) are

widely available. An ideal probe to interact with a GO surface (Figure 2A) in aqueous dispersion would include (Figure 2B) a flat aromatic moiety for hydrophobic interaction with graphene surfaces, and a hydrophilic group to ensure solubility (and modulate interaction with polar groups). Such a design mirrors that of some reported graphene 'dispersants'²⁹ (surfactants to mediate aqueous dispersion of insoluble graphene flakes), including the molecule illustrated in Figure 2B (P1).³⁰ Although fluorescence is not relevant to dispersants, we show here that GO interaction quenches these molecules' emissions (Figure 2C). A number of species already known to interact with GO surfaces, are also fluorescent, offering similar promise as probes.²⁶

For this study, we assembled a library of probes **P1-P10** (Scheme 1), comprising a range of known dispersants and other fluorescent probes. Most are



Scheme 1. Library of GO-interacting probes.

Table 1. Collection of commercially available GO materials.

Sample	Sold as	Flake Size (μm^2) ^c	O/C ^a	I _D /I _G ^b	I _{2D} /I _G	IR 'flat' ^d	Data consistent with 'consensus' GO?
GO[A]	GO	4.93 (± 0.43)	0.44	1.27	0.22	n	✓
GO[B]	Ammonia-functionalised GO	2.31 (± 0.28)	0.31	1.37	0.20	n	✗
GO[C]	GO	0.86 (± 0.25)	0.47	1.19	<i>negligible</i>	n	✗
GO[D]	GO	2.58 (± 0.26)	0.05	0.30	0.27	y	✗
GO[E]	GO	0.44 (± 0.12)	0.47	1.38	0.17	n	✓
GO[J]	Carboxylic acid enriched GO	0.95 (± 0.49)	0.45	1.23	0.29	n	✓
GO[K]	GO	0.89 (± 0.24)	0.46	1.40	0.27	n	✓
GO[L]	GO	4.63 (± 0.32)	0.32	0.26	0.13	y	✗
GO[M]	GO	4.70 (± 0.29)	0.12	0.06	0.39	Y	✗
GO[N]	GO	4.73 (± 0.29)	0.58	1.36	<i>negligible</i>	N	✗

Full characterisation data and acquisition details available in Supplemental Information. ^a Elemental ratio of oxygen to carbon (O/C), calculated from XPS survey (I_O/I_C) in Raman spectra. ^c Flake Size distribution taken from SEM images. ^d Is IR spectrum featureless, inconsistent with material being graphene oxide (“✓ spectrum features consistent with GO structure”).

commercially available, and the remainder (**P1**, **P5**) were readily synthesised in few steps by established procedures (see Supplementary Information).^{30,31} All can be seen to be fluorescent (see Supplementary Information, Section 2.2), and their fluorescence is quenched on interacting with GO.²⁸

Library of GO commercially available materials.

To test our assay, we purchased a diverse selection of commercially available GO materials from a range of suppliers. Along with 8 samples sold as graphene oxide, we also added samples described, respectively, as “Ammonia Functionalised Graphene Oxide” (**GO[B]**), and “Carboxylic acid enriched Graphene Oxide” (**GO[J]**). Most samples were purchased as dispersions; those which were bought as flakes were dispersed in water.

We performed a range of orthodox characterisation on our library of GO materials (XPS, Raman, SEM, IR, UV), summarised in Table 1 (see Supplementary Information, Section 4, for full results). Unlike graphene, which should have a single structure, varying only in dimensions and defects, graphene oxide materials can vary in a variety of parameters, while remaining graphene oxide: in particular in the nature/patterning of surface groups (acid, alcohol, epoxide). Here we refer to some ranges here as ‘consensus’ GO, based on a recent survey,¹² and our own data; this is an

arbitrary label (see below). From XPS elemental analysis, we see that O/C ratios vary considerably in our GO collection, and some are inconsistent with consensus GO ranges (e.g. **GO[M]**, **GO[D]**, with very low oxygen content). As expected, significant amounts of nitrogen were observed in XPS survey of the ammonia-functionalised GO (**GO[B]**; 2.6% N), with negligible amounts observed in most other samples (<0.6, which may reflect traces of buffers). By SEM we observe a range of flake sizes, while some materials do not appear homogenous, or do not appear to be composed of 2D flakes (see Supplementary Information, Section 4.5, for images). By Raman spectroscopy we note that some Raman I_D/I_G ratios are inconsistent with consensus GO (e.g. **GO[D]**, **GO[L]**, **GO[M]**), and some samples stand out as lacking observable I_{2D} bands (e.g. **GO[C]**, **GO[N]**). IR spectra of some samples lack features consistent with GO structure (e.g. **GO[D]**, **GO[L]**, **GO[M]**). Measurements for some GO materials, however, fall in the ranges more typical of GO (e.g. **GO[A]**, **GO[E]**, **GO[J]**, **GO[K]**), and these we will refer to as ‘consensus GO’ for the remainder of this paper, denoting the range of materials for which we intend to optimise our assay. Importantly, we note that many of these properties vary orthogonally, with no simple relationship apparent, meaning rapid measurement with a single established method is unlikely to differentiate materials clearly.

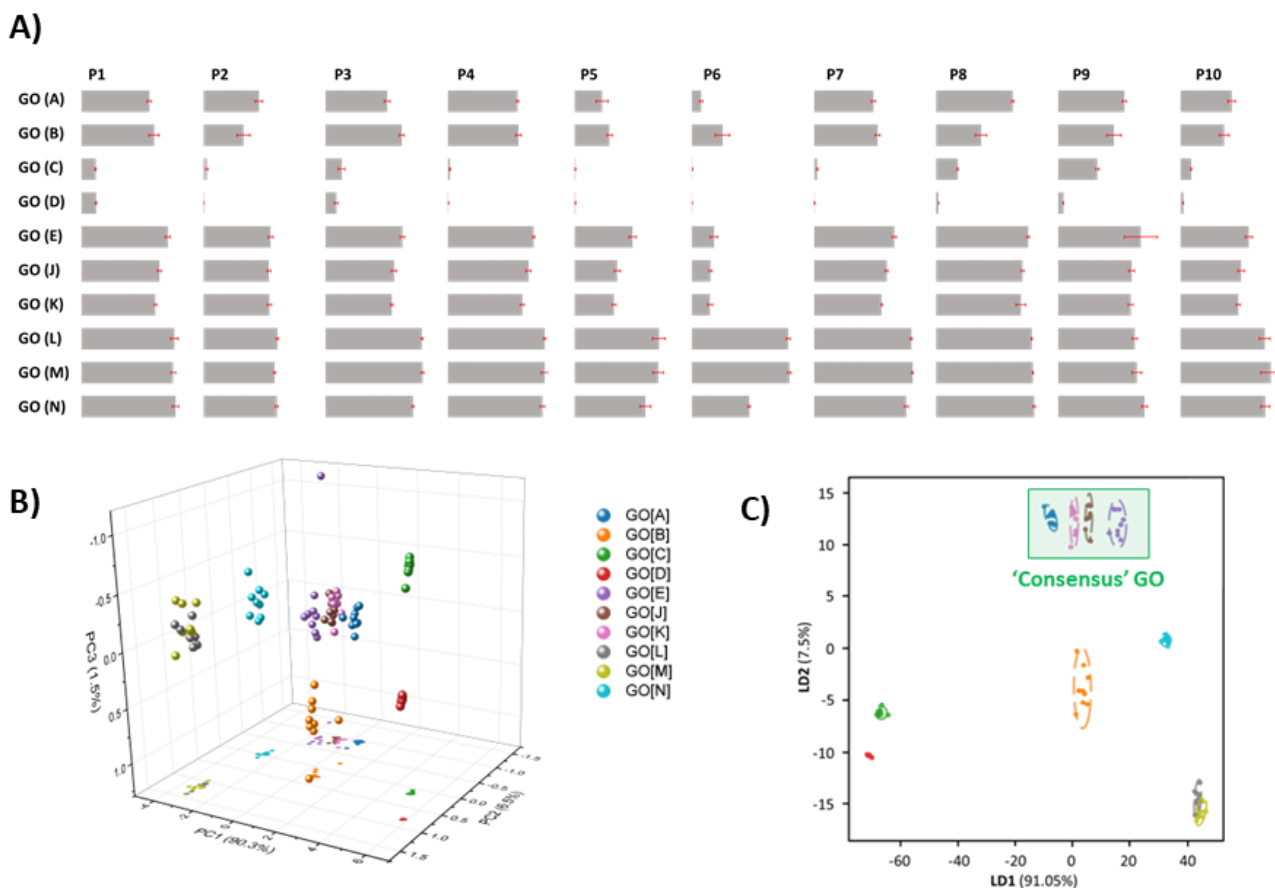


Figure 3. Multivariate analysis of GO library 'Interactional Fingerprint' data provides qualitative information on GO materials.

(A) Normalised fluorescent response from each probe to each GO sample. [see Table S1 for excitation/emission wavelengths; average readings from 9 measurements; error bars represent one standard deviation; see Table S2 for full data].

(B) 3D PCA analysis plot of interaction data from all probes (**P1-P10**) with GO library, representing ca. 98.3% of data variance. [Note: PCA is an unsupervised technique. Colours were added for display, and the identity of samples is not included in processing.]

(C) LDA analysis of interaction data from all probes (**P1-P10**) with GO library. The area in which 'consensus' GO samples fall is marked: a small subset of LDA space, distant from other samples observed to be more distinct by orthodox analysis.

[In panels B and C, 'points' represent the response of a single reading; ellipses represent a 95% confidence limit for each GO material, calculated after multivariate analysis is completed, representing variation on repeated measurement]

Applying the Probe Array to map GO materials' Interactional Fingerprints.

To establish reasonable conditions to apply our array, we performed small scale tests to establish conditions in which all probes could be observed to interact to some extent with a small number of consensus GO sample dispersions without completely quenching fluorescence, as well as altering probe concentration, GO concentration, pH, ionic strength, and GO handling (e.g. 'settle times', following mild agitation, during which a dispersion is homogenous and the response is reproducible).

Under these assay conditions we then surveyed the response of our full range of probes to our GO library, with responses shown in Figure 3A: the GO

materials' 'interactional fingerprints'. Most of the GO samples produce distinct responses (degrees of probe quenching). That responses vary orthogonally reflects a range of properties. For example, the response of **P2** to **GO[K]** and **GO[L]** is similar, whereas the response of **P6** to the same materials is markedly distinct. It is difficult to interpret this multivariate data set directly. Applying Principal Component Analysis (PCA) to deconvolute out 'fingerprint' data, we can map our materials in a 3D plot (Figure 3B; see Figure S1 for simple 2D representation). PCA is an unsupervised method (it uses no data on sample identity), yet in the PCA plot we see that dissimilar materials are distant and clearly resolved, and similar materials (by conventional analysis) are grouped together.

Materials differ in all three principal components independently (e.g. **GO[C]** and **GO[D]** are close in *PC1* and *PC2*, but more distant in *PC3*, reflecting their very distinct surface chemistry), again demonstrating that this mapping is not a response to a single attribute, but a qualitative ‘summary’ of the materials’ properties.

Linear Discriminant Analysis (LDA) is a supervised method, which incorporates information on which group each data point belongs to (**GO[A]**, **GO[B]**, etc) to optimise the resolution of the materials. Applying LDA (Figure 3C) provides greater resolution between the different materials, such that almost all samples are clearly resolved in two dimensions (repeated stratified k-fold cross validation suggests >97% classification accuracy). Even in a simple 2D plot, all samples characterised as resembling consensus GO (see Table 1) occupy one area of the plot, which is clearly distinct from the space occupied by other materials.

While it is far more accessible than conventional characterisation, obtaining readings of responses

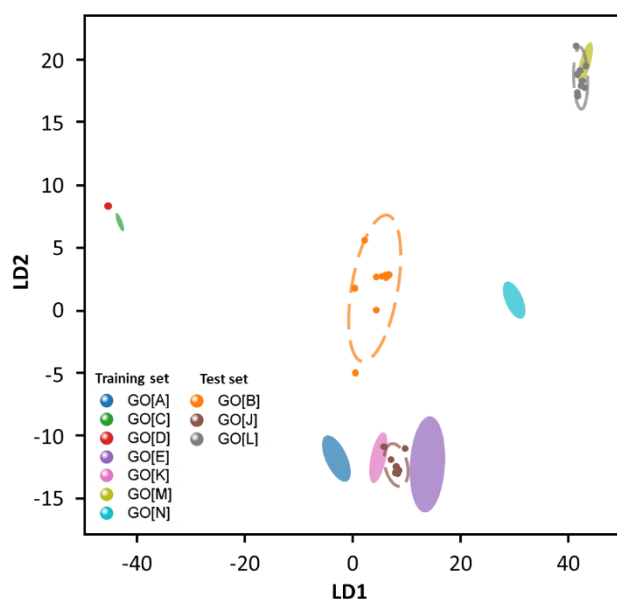


Figure 4. Practical comparison of ‘new’ materials to a ‘test’ or calibration set of GO. LDA analysis of interaction data from a reduced range of probe (P2, P6, P7) with a ‘test’ (or calibration) subset of the GO library (**GO[A]**, **GO[C]**, **GO[D]**, **GO[E]**, **GO[K]**, **GO[M]**, **GO[N]**), represented as filled ellipses. This LDA model is then applied to a ‘test’ set of GO materials, represented as ‘points’, which fall in areas adjacent to similar materials. [Ellipses represent a 95% confidence limit for each GO material, calculated after analysis is completed, representing variation on repeated measurement; ‘Points’ represent the response of a single reading]

to our full library of probes (**P1** to **P10**) still requires considerable labour (liquid handling/pipetting). Reducing the range of probes used, we find that similar LDA plots are observed (see Figure S2): even using 3 probes (**P2**, **P6**, **P7**), yields a qualitatively similar result, while requiring fewer manipulations.

A practical QC method should to allow a GO material user to ask “*Is this material like other batches?*” when obtaining new material, or performing quality control to compare a new batch of material with others.¹¹ To simulate this, we split our data (on responses to only three probes, **P2**, **P6**, **P7**) using responses to most GO sample data as ‘calibrants’ to train an LDA model, and reserving **GO[J]**, **GO[L]**, and **GO[B]** as ‘test’ samples. Training an LDA model with this reduced set produced a plot similar to other LDA analyses (filled ellipses, Figure 4). Applying this model to the test set, we see that all three samples are placed in an area of the resulting plot to reflect their properties (data in unfilled ellipses, Figure 4): **GO[J]** falls between the similar ‘consensus GO’ samples **GO[E]** and **GO[K]**; the ammonia functionalised GO sample **GO[B]** is discriminated from all of these; and the outlying sample **GO[J]** remains identifiable as clearly distinct. For consumers or producers of ‘consensus GO’ materials, a new batch of material not falling into the appropriate range, but fitting into the range of material sold as “graphene oxide”, would be clearly observed.

Applying the fingerprinting approach to extract quantitative information.

Qualitative analysis is sufficient for many QC needs, however in some cases quantification of a systematically varying property is necessary: particularly when performing modification of a material. To test this, we produced a series of modified GO samples from the same starting material, in which differing proportions of surface alcohol groups have been esterified (Supplementary Information, Section 5), and measured the degree of modification using an established method (see Supplementary Information). Performing our assay to the resulting GO materials (**GO[Mod-A]** to **GO[Mod-E]**, w/**P1** to **P5**), and subjecting the resulting ‘interactional

fingerprint' data to PCA reveals a progressive shift in *PC1* as degree of modification increases (see Figure S11). Splitting materials into training (most materials) and test sets, performing PCA on all, and plotting mean *PC1* against the degree of surface modification for our test set, we observe a linear relationship between degree of modification and *PC1* response (see Figure S11). Using this relationship, we are able to estimate the degree of modification of the test material (**GO[Mod-D]**, estimated as 39.5% modified; determined as 38% modified). While we note that this series of materials varies systematically only in the degree of modification, we may tentatively consider this a demonstration of the potential for this approach to rapidly quantify surface modification.

DISCUSSION AND OUTLOOK

We have shown that obtaining an 'interactional fingerprint' of GO material dispersions by applying an array of suitable fluorescent probe molecules can provide useful qualitative information on GO materials. Leading commentators have discussed the need for "*rapid and inexpensive*" QC methods, which "*can be performed on the factory floor*" to "*identify changes in the material*", and which need not provide all the information yielded by gold standard methods.¹¹ We propose that our fingerprinting approach is a promising candidate for this role, allowing us to rapidly differentiate 'consensus' GO from other samples. We note that our demonstration of this requires only simple apparatus/materials (pipettors, microplate reader) and commercially available materials (probes, reagents, GO standards), making it accessible. An assay in which nanomaterials are handled as aqueous dispersions is also preferable for safety reasons.

The demonstration of the fingerprinting approach we present here is optimised for the group of materials we have arbitrarily labelled as 'consensus GO', and allows us to distinguish between these and other "GO" materials which are available commercially. Given relevant material samples ('standards'), this kind of assay can readily be tuned for a range of challenges (by altering probe choice, probe concentration, GO concentration, pH, ionic

strength, etc). This may be helpful, for example, to determine finer variation between '*in spec*' and '*out of spec*' materials, as might be required by manufacturers for QC, as well as distinguishing between different classes of GO/GBM, or other materials characterisation challenges.

Beyond QC testing, many of GO's applications depend on surface properties, such as sequestration of pollutants,³² metal extraction,³³ compounding in hybrid materials, photocatalysis, etc. Indeed, GO surfaces are often used as a probe for other analytes, or platform for sensing.³⁴ Our approach is a reversal of this, understanding GO by its recognition properties, and we propose that such an approach may be well-suited to shed new light on a wide range of materials' surface properties. Such developments may require the availability of reliable standards, and complex data processing (e.g. machine learning), but promise a more direct means to assess materials' surface chemistry than orthodox microscopy- and spectroscopy-based characterisation.

METHODS

All experimental procedures are detailed in the Supplementary Information.

The commercially available graphene oxide samples were all obtained in the UK, from companies in the UK, Europe, and adjacent countries, and analysed without further purification other than protocols described.

Resource availability

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Andrew Surman (andrew.surman@kcl.ac.uk).

SUPPLEMENTARY INFORMATION

Supplementary Information file contains experimental procedures, Figures (S1 to S17), and Tables (S1 to S5).

ACKNOWLEDGMENTS

All authors thank the EPSRC for Impact Acceleration funding (IAA2022AIA01) for financial support, and King's College London for access to facilities; EAS thanks the Engineering and Physical Science Research Council Doctoral Training Programme for PhD funding; EC thanks King's College London for PhD funding. The X-ray photoelectron (XPS) data collection was performed at the EPSRC National Facility for XPS ("HarwellXPS"), operated by Cardiff University and UCL, under Contract No. EP/Y023587/1. We are grateful to Dr Mads Berghold and Peter Pilecki for assistance with Raman spectroscopy, and to Holly Pearce and Dr Shannon Stockdale for assistance with SEM microscopy. We also thank Dr Robert Menzel, University of Leeds, for bringing the challenge of rapid GO characterisation to our attention, and Dr Andrew Pollard, National Physical Lab, for helpful discussions as we have developed this concept.

AUTHOR CONTRIBUTIONS

AJS conceived the project; AJS and BIVA designed experiments and wrote the paper, both with contribution from all authors (IA, EC, HL, EAS); IA established proof of concept for the assay; IA, BIVA, and HL performed probe synthesis; all authors

performed data analysis; EC, IA, and AJS wrote code for data analysis; IA, HL, and BIVA performed experiments to develop the assay procedure; BIVA performed modified GO synthesis; BIVA and EAS led characterisation of the GO library by standard methods; AJS and BIVA supervised the team.

DECLARATION OF INTERESTS

King's College London have submitted a patent application covering aspects of the work reported here (WO2023209389 **2023**).

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