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Shear perfection?

A new shear-driven technique could make graphene quality more reliable. **Dr Jason Stafford** at the University of Birmingham and **Dr Sofia Marchesini MIMMM** at the National Physical Laboratory, UK, report.

The hype around graphene has spread well beyond beingexfoliated with scotch tape in a laboratory, to being produced at a scale of tonnes per year by companies globally. Graphene is now embedded in many commercial productsto exploit its excellent mechanical strength, for example, as reinforcement in concrete, tyres and bicycle frames, resulting in increased lifetimes without additional weight.

Despite the widespread interest in this 'wonder material' , in general, its real-world application potential is yet to be fullyrealised. Part of the reason behind its slow uptake lies with limited and inconsistent characterisation data. This is critical to give users confidence in the material being purchased and allowaccurate comparison between different suppliers.

In fact, the properties of commercial materials, particularlythe number of 2D atomic layers, can vary greatly depending on the production method, with many materials containing unexfoliated graphite.

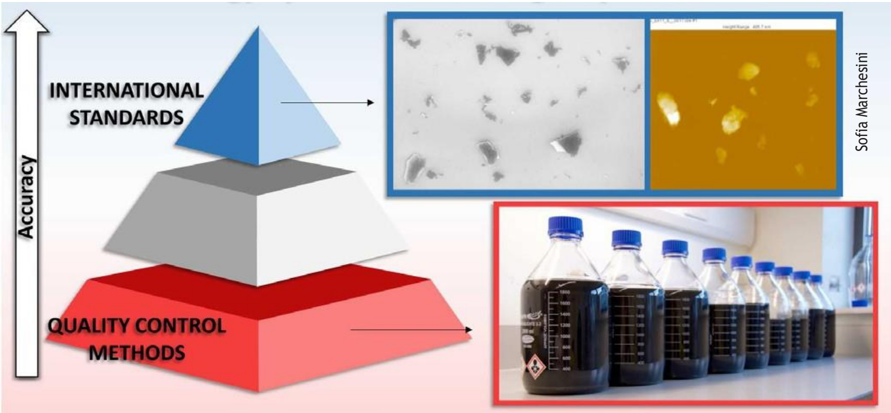
Different applications require different optimised material properties, making it important that products can be fully characterised to advance such technologies. Until recently, therehas been no agreed standardised methods to characterise the materials, however, an International Standard, led by the National Physical Laboratory – ISO TS 21356-1 – has recently been published.

These guidelines provide details for measuring the lateral sizeand number of 2D atomic layers in graphitic particles combining microscopy, spectroscopy and scanning probe techniques to improve the repeatability and confidence in the measurements used for characterisation.

However, current standardised measurement techniques suffer from a range of disadvantages. They can be expensive, lengthy, and only measure a limited number of particles. It means the techniques are unable to be applied for rapid qualitycontrol of materials produced in large quantities by graphene manufacturers directly on the factory floor.

This is seen as a major drawback in the manufacturing industry, which is limiting the advancement of graphene- based technologies. Technology companies balance the risk ofintroducing new materials and processing facilities into their production lines against the product innovations and performanceimprovements that materials such as graphene can realise. Without a suitable metrology framework to ensure material qualityand repeatability, the level of risk will remain too large for many.

New methods must be urgently developed to measure the yieldand number of 2D layers in graphitic products produced at scale. Quality control methods capable of characterising the number of graphene layers would allow manufacturers to control their production process promptly and potentially *in situ*, ultimately improving the quality of their products for a specific application.



Metrology pyramid – measuring graphene yield

Above: Current challenges in the graphene manufacturing industry aroundthe lack of quality control methods for characterising a number of layers

Strong character

One of the most common methods for producing graphene at scale is liquid shear exfoliation. This is when graphite is added to a solvent and exposed to mechanical shear forces, causing particles to break and layers to peel apart. This methodenables the production of large quantities of graphene with a low number of defects, but also generates wide particle size distributions and a number of atomic 2D layers.

Materials produced in liquid dispersions can be advantageousfor applications such as printing and spray coating. However, it is inconvenient when using existing characterisation techniques that require dry samples. Moreover, wide particle size distributions mean that many particles must be characterised toobtain a truly representative picture of a material's properties.

In this context, a characterisation technique has been developed at Imperial College London, UK and the University of Birmingham, UK – (WO/2021/019228). It deploys an optical transmission-reflectance approach to measure production rateand the number of atomic layers of 2D graphitic materials in real-time.

The method addresses two key barriers for scalable production monitoring and quality control. The first is the challenge of performing measurements *in situ*. Liquid exfoliationis a top-down technique that starts with a mixture of solvent and graphite precursor particles and finishes with the same components plus the high-value graphene product. Established techniques that measure graphene yield and quality are performed *ex situ*, relying on time consuming post-processing steps to isolate these materials for subsequent analyses. The need to do this inherently removes any possibility of obtaining live measurements during material processing.

The second barrier is cost. It may be possible to overcomesome of these technical challenges by adapting existing lab characterisation equipment, but this may not be enough to realise quality control at industrial scales, and certainly not along the entire value chain from material production to point-of-use in an application.

Current methods use equipment that has low portability, and typically requires high capital and operational expenditure that is prohibitive to most. Alternative, low-cost methods are necessary to monitor graphene production and quality control at scale.

During the exfoliation of graphene, the optical characteristics of the liquid mixture change over time, and the dispersion appears darker as more material is produced. Although partially exfoliated graphite influences this, we found a significant contribution is due to the unique optical characteristics of graphene itself.

Even though a single atomic layer of graphene is almosttransparent (~98%), when trillions of single- and few-layer nanosheets are in dispersion, the cumulative effects of light absorption lead to an opaque liquid.

Useful information can be revealed about graphene by looking at its absorption spectrum from ultra-violet to visibleand near-infrared wavelengths. The amount of material in a liquid dispersion can be determined by measuring absorbanceat a wavelength where graphene's spectrum is insensitive to nanosheet thickness (660-900nm). Whereas the shape of the absorbance spectrum in the ultra-violet to visible region is sensitive to nanosheet thickness and can give information aboutthe average number of atomic layers.

The newly developed transmission-reflectance spectroscopy approach captures this information non-invasively during the shear exfoliation process. This removes time-consuming physical sampling, post-processing and material preparation steps currentlyemployed. In doing so, instantaneous measurements of productionrate and average layer number can be obtained without interferingwith the hydrodynamics of the shear exfoliation process.

Through the lens

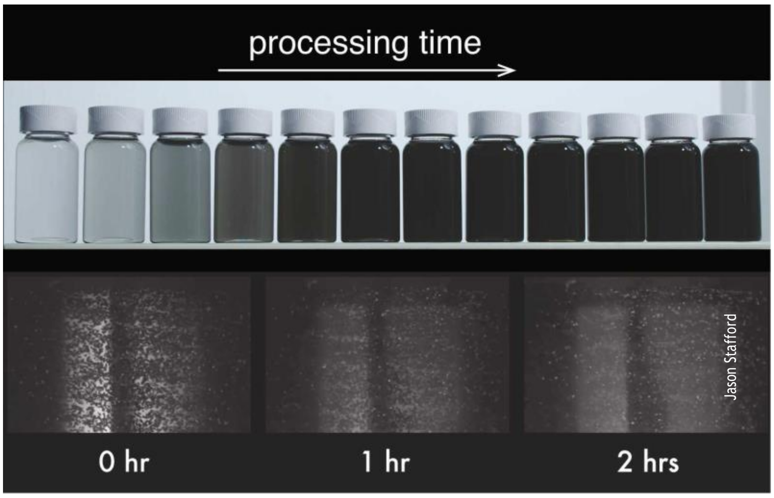
Achieving this cost-effectively, however, requires a move away from traditional lab spectrophotometers that cost thousands of pounds. Instead, we focused on developing a spectroscopy technique out of the ubiquitous materials found in chemical process equipment, while also taking advantage of the rapid advancements in sensor-on-chip technologies.

Stainless steel and borosilicate glass windows in the shear exfoliation process are used as optically participating components in the transmission-reflectance approach. Theyprovide a diffusely reflecting background and a transmissive boundary that permit incident and reflected light to travel from the light source, through the absorbing liquid dispersion, and into an externally mounted online sensor.

A light emitting diode serves as a broadband white light source and links to the sensing system via an electronic shutter. This sensing system comprises a land grid array (LGA) optoelectronics package with built-in aperture, internal lensand multi-spectral photodetectors developed by sensors manufacturer ams AG, in Austria.

For graphene dispersions, it is possible to determine concentration and average number of atomic layers without measuring the complete spectrum in high resolution. Removing the need for nanometre or sub-nanometre wavelength resolutionleads to a drastic reduction in cost over laboratory methods without compromising on measurement accuracy. Importantly, itopens up the use of highly portable sensor-on-chip technologiesfor graphene characterisation that only cost a few pounds.

This multi-spectral sensor integrates Gaussian filters on complementary metal–oxide–semiconductor (CMOS) silicon using ams AG's nano-optic deposited interference filter technology. The resulting photodiode array contains individual channels that are sensitive across a 20-40nm bandwidth and centred at discrete wavelengths, spanning the ultra-violet to near-infrared region. This allows us to acquire transmission- reflectance data across the graphene spectrum simultaneously,capturing sufficient information to obtain production rate and layer number in real-time.



Above: Liquid dispersions containing few-layer graphene (top) and high-speed images taken during shear exfoliation of graphite precursorparticles (bottom)

Real-time results

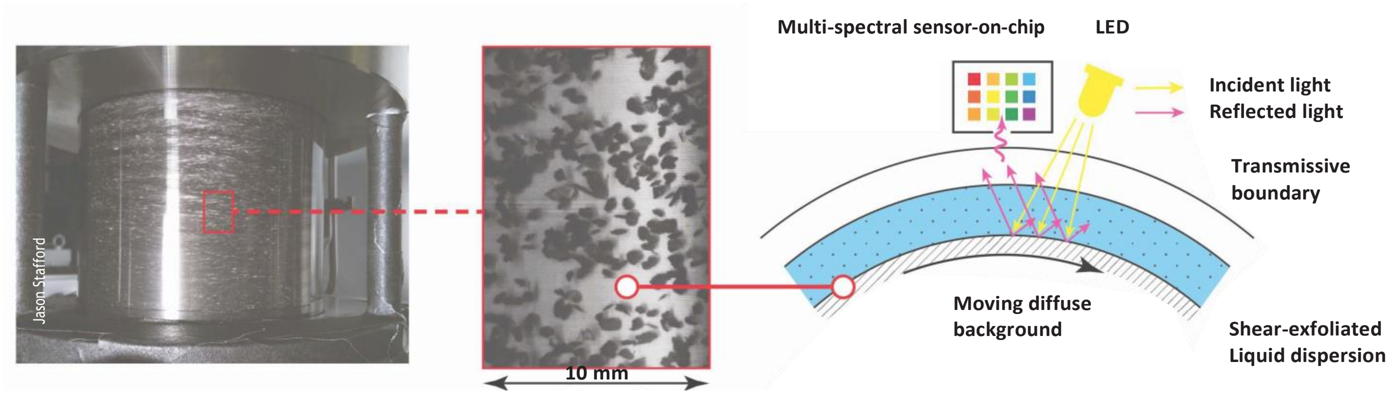
From an industrial standpoint, real-time monitoring of graphenedispersions will be hugely advantageous for managing resource efficiency and environmental sustainability of large process volumes. Live production rate information can guide operating parameter and solvent choices, indicate when a process is not performing as intended, determine optimal mixing conditions ofcomposites, or identify the exact time when a batch should be changed out to maximise material throughput.

Being able to monitor the average layer number of particlesin graphene dispersions ensures quality control and tuning of material properties, taking a step towards materials-by-design. Low-cost, high-portability graphene monitoring devices could make scale-out to every production line a real possibility. This would facilitate the creation of batch traceability records and certifications for global material resource flows between producers, distributors and application integrators.

A key requirement for scalable quality control methods becoming a reality is validation and verification against more accurate standardised techniques to understand sources of uncertainty. The reproducibility of new quality control methods must also be assessed by performing interlaboratory studies on selected samples. These efforts are necessary to establish accurate and reliable quality control characterisation methods for the graphene industry. Ultimately, such techniques and measurement protocols must be compared through the international interlaboratory comparisons of the Versailles Project on Advanced Materials and Standards (VAMAS), so they can be implemented into international standards (such as ISO) toenable broad comparison between graphene products.

Commercial validity

The combined effort of industry, academia and national laboratories is required to realise, reliable, yet affordable, methods for the characterisation of the number of 2D atomic layers in graphene products. The accurate determination of graphene properties will instill confidence in commercial materials and ultimately lead to the realisation of graphene’s fullpotential in real-world applications.



Above: The liquid exfoliation process (left) shears microscale graphite particles dispersed in a solvent (middle) to produce graphene. This process is monitored in real-time using an online multi-spectral transmission-reflectance approach (right)