Publishable Summary for 19NRM04 ISO-G-SCoPe
Standardisation of structural and chemical properties of graphene

Overview

The overall aim of this project is to validate and standardise measurement and characterisation methods for the chemical and structural properties of graphene in powders and liquid dispersions for industrial applications. This will overcome a "what is my material?" barrier for both users and producers leading to well-characterised highly tailored graphene, graphene oxide and chemically functionalised graphene. This will maximise innovation and competitiveness of European industries across the supply chains in multiple sectors including the energy sector, photovoltaics, lithium ion batteries, flexible electronics, composites, consumer products, novel coatings, clothing, automotive and aerospace industries.

Need

Graphene and related 2D materials are predicted to make a major impact in many technology areas, either through incremental advances via current material replacement, or via disruptive changes. However, the uptake of these materials into commercial products is hindered as industrially produced "graphene" is often incompletely or not correctly characterised by the 100+ suppliers. This is acknowledged as the single biggest issue by graphene companies, suppliers and standards bodies [e.g. ISO TC229 (nanotechnologies), BSI NTI/1 (nanotechnologies) and BSI UK-China JWG on graphene standardisation]. Issues include structural determination of the material as graphene or graphite, how many layers are present and what is the flake size distribution in different batches. Chemical determination issues include the amount of oxygen present (for graphene oxide and reduced graphene oxide), impurities and functionalisation. There are no standard ways to measure these properties for the industry to take the material from the laboratory to large-scale production.

Industry is rushing to develop their own internal measurement procedures to obtain reproducible results for their process optimisation and for external sales. These remain poorly accepted by their peers and competitors. Before the project started, there were standardisation documents progressing through ISO TC229/IEC TC113 and ASTM E56 but these were either overview technical reports, focused on electrical measurements or other issues. They did not contain validated measurement protocols for structural and chemical properties. There are also no European Standards. European industries require international documentary standardisation of structural and chemical methods to characterise graphene validated via pre-normative VAMAS international interlaboratory testing. This will allow end-users to compare technical datasheets of different commercially available ‘graphene’ products worldwide. This will instil confidence and allow faster innovation and increased R&D productivity, as end- users will only need to test a few materials rather than hundreds. These end users will be able to match highly tailored 2D materials to performance requirements. Standardised characterisation procedures are also required for companies needing to comply with new nanomaterials regulations and in particular registering graphene nanoforms in the REACH register [ECHA, 2017 Appendix R.6-1] allowing reliable toxicity testing of different products on the market.

The aim of this project is to build on the established work items at ISO and IEC in terminology and overview standards and add robust metrology, methodology and supply validated measurement methods and supporting data. This will lead to the publication of three industry critical ISO standards via ISO TC229 which will become adopted as European standards via CEN TC352.

Objectives

The overall objective of this project is to validate and standardise measurement and characterisation methods for the chemical and structural properties of graphene in powders and liquid dispersions for industrial applications.

The specific objectives of the project are:

1. To lead and provide a contribution to the initial and revised publication of “ISO DTS 21356-1 Nanotechnologies – Structural characterisation of graphene: Part 1: Graphene from powders and liquid dispersions”. The contribution will focus on measurement methods for the characteristics of graphene flakes in order to verify measurements made on commercial graphene flake products.
2. To lead and provide a contribution to the development of ISO/PWI 23359 "Nanotechnologies - Chemical characterisation for graphene in powders and suspensions" and to lead and provide a contribution to ISO/PWI 23879 "Nanotechnologies – Structural characterisation of graphene oxide flakes: thickness and lateral size measurement using AFM and SEM”. The contribution will focus on developing validated quantitative measurement methods.
3. To provide a contribution to pre-normative international interlaboratory studies in VAMAS TWA 41 (graphene and related 2D materials), leading and participating in characterisation studies focused on structural and chemical properties using, XPS, AFM, Raman, and SEM techniques.
4. To work closely with the European and International Standards Developing Organisations, and pre-normative organisations, and the users of the Standards they develop, including the Graphene Flagship, to ensure that the outputs of the project are aligned with their needs and incorporated into Standards at the very earliest opportunity.

Progress beyond the state of the art

When the project started, there hadn’t been any published international standards on validated measurement and characterisation methods for the structural properties of graphene and no other source of validated standard operating procedures to use in industrial applications. There has been the first version of the terminology standard on graphene and related 2D materials (ISO TS 80004-13) and an overview ISO technical report (ISO/TR 19733;2019) that provides a matrix listing key properties of graphene to measurement techniques. The consortium is helping to lead the update of the terminology standard including new terms.

The first version of ISO TS 21356-1 was published in March 2021, with the consortium providing final editing. This is a dual logo ISO TC229 and IEC TC113 publication. This document provides a flowchart of methods to characterise graphene. This along with the terminology standard allows users to determine what is graphene and then measure it. However, critically in this first version, it does not provide validated measurement protocols but only example methods as informative annexes as they have not been validated though VAMAS interlaboratory studies. This project will provide industry with its much-needed validated measurement methods for the structural characterisation of commercial powders and dispersions containing graphene flakes. These will form the centrepiece of an updated revision of ISO TS 21456-1 that will contain validated methods to determine essential properties that industry who are supplying, purchasing and using graphene require. This includes average flake size and flake size distribution, number of layers, flake thickness and level of disorder. The methods will be standardised using the techniques of SEM, Raman spectroscopy and AFM. The consortium will produce the updated draft document with these methods as normative sections in the standard.

At the start of the project, there were no international standards to measure the chemical properties of graphene, functionalised graphene and graphene oxide (GO). There were also no international standards for characterising the structural properties of graphene oxide, as well as no graphene or 2D materials specific surface chemical analysis standards for example using XPS. Functionalised 2D materials are readily available to purchase but the products are uncharacterised by validated methods and hence are very likely to have different chemical composition to those that are expected. The consortium are world-leading on the development of the first international standards in a) chemical characterisation of graphene/functionalised graphene and graphene oxide and b) graphene oxide structural characterisation. Methods will be developed, tested in-house and then validated via international interlaboratory studies on: i) graphene oxide measurement using SEM, ii) graphene oxide and functionalised graphene using XPS. This along with the consortium’s metrological knowledge in AFM will be used to lead and input into the writing of the new work item proposals for the two ISO standards on graphene oxide measurement using SEM and AFM and chemical characterisation of graphene, graphene oxide and functionalised graphene.

The principal measurands of graphene nanoplatelets that AFM measures are the lateral flake size and thickness. Current uncertainties for measurements undertaken in industry are approximately 10 % and 20 % respectively. This is due to poor scanner calibration and image analysis protocol as well as sample preparation

and general measurement protocol. the consortium will lead and drive progress in 4 pre-standardisation interlaboratory studies in VAMAS TWA 41. These will be designed so as to write, test and improve the protocols that will form the basis of the current ISO standards under development or to be revised, as well as reducing the uncertainties in all the measurements in industry based on the key issues: AFM uncertainties will be reduced to around 1 % for lateral size measurement and 5 % for thickness for measurements in industry. SEM uncertainty measurements in lateral flake size will be reduced to approximately 1 %. Raman spectroscopy uncertainty measurements in the number of layers will be reduced to one layer. XPS uncertainty measurements will be reduced to around 10% for NMIs and around 20 % for industry. These levels of uncertainties will be achieved via well-documented protocols for AFM, SEM, Raman spectroscopy and XPS for measurement and measurement analysis as well as guidance on general instrument calibration.

Results

1. "ISO DTS 21356-1 Nanotechnologies – Structural characterisation of graphene: Part 1: Graphene from powders and dispersions".

This ISO technical specification specifies the sequence of methods for characterising the structural properties of graphene flakes using a range of measurement techniques. The properties covered are the number of layers/thickness, lateral flake size, the level of disorder, layer alignment and specific surface area. The first version of this standard did not include standardised methods and the consortium led the final editing and proof-reading of the document. ISO TS 21356-1 was published in March 2021 as the first graphene measurement standard. The consortium wrote a review paper summarising the standard with 10 international co-authors and published in the Nature Reviews Physics Journal. Importantly, in the first version of the standard, measurement protocols are only included as informative annexes, as they have not been validated via VAMAS interlaboratory studies. The consortium is currently developing these essential VAMAS interlaboratory studies, particularly here involving SEM and AFM measurement. The consortium is developing and validating these methods whilst reducing uncertainties. The standard will then be revised within ISO TC229, such that it includes the normative measurement protocols.

2. ISO/PWI 23359 'Nanotechnologies - Chemical characterisation for graphene in powders and suspensions' and ISO/PWI 23879 'Nanotechnologies – Structural characterisation of graphene oxide flakes: thickness and lateral size measurement using AFM and SEM'

Before the project started, these draft standards, led by the UK and UK /China respectively, were at the preliminary work stages and had been for approximately 18 months. Progress was hampered, due to the need for the methods to be validated using international interlaboratory studies. The project partners started writing the draft standards in the first year. For ISO/PWI 23359, this involved drafting the entire document, including a flow chart, general sections and measurement method sections on XPS, ICP-MS, TGA and FTIR. ISO experts from China and Australia wrote the last three, (ICP-MS,TGA and FTIR) with significant editorial contributions by the consortium. The first draft was written, and ISO TC229/JWG2 gave the go-ahead for a new work item ballot. This ballot was held between 15 July to 8 October 2021. The proposal attracted strong support and received comments/support from countries around the globe including Canada, US and France. Ballot comments were discussed at the ISO TC229/JWG2 meetings in November 2021 and May 2022.

For ISO/PWI 23879, the draft was written in collaboration with NMI, China. This has undergone new work item ballot and has been approved as an ISO work item. The consortium will progress the documents through the ISO process in collaboration with NIM.

3. Pre-normative international interlaboratory studies in VAMAS TWA 41 (graphene and related 2D materials)
At the start of the project, within VAMAS TWA41, there were currently 6 planned or current VAMAS graphene interlaboratory studies, with only 4 on graphene flakes. This project is providing the focus and drive to run 4 new interlaboratory studies in a short period of time on AFM/SEM and Raman spectroscopy of graphene flakes, SEM of graphene oxide (GO) and XPS of chemically functionalised graphene leading to validated methods and reduced uncertainties. For each measurement technique for industrial use, the uncertainties in measuring the chemical and structural properties (e.g. flake size, thickness, number of layers) will be reduced from generally 10-50 % by at least a factor of two depending on the measurand and technique. So far measurement protocols are being developed and tested and improved. Importantly the samples have been sourced and sample preparation is being optimised. Excellent repeatable samples are the key to a successful interlaboratory study, so time is being spent to produce the best samples possible. This has included the manufacture and testing of specially produced substrates with fiducial markers and a calibration grid for SEM

and AFM calibration checking. Much work has been undertaken on optimising the deposition procedure for graphene flakes onto these substrates to have well-separated flakes. This has been solved and samples produced including those on the special substrates. The protocol is now being finalised and participants invited before launching the study.

For XPS analysis, work has been ongoing to understand differences between the analysis of pellet samples and those of loose powder. In early 2022, the protocols and samples were tested in small test interlaboratory studies involving project partners. This is to check and improve the protocols. New test material was produced and supplied by Haydale and differences between high energy (HAXPS) and normal (XPS) investigated by BAM and NPL on the material. The XPS study will launch in September 2022.

For Raman spectroscopy, initially multiple issues with the initial test material were found. After a few iterations, new material was produced by NPL (chemically exfoliated graphene) and by the university of Manchester (mechanically exfoliated few layer graphene). Both of these are being tested by INRIM prior to launching the interlaboratory study.

For GO analysis using SEM, commercial GO has been sourced as the reference material. BAM are investigating and improving the GO deposition procedure in order to produce well separated GO flakes of appropriate density for SEM measurements.

Impact

The consortium is putting impact at the centre from the outset and throughout the duration of the project. There will be strong engagement with key stakeholders via the interlaboratory studies and the accompanying standards development. The consortium is partnering with the Graphene Flagship project and industry associations such as the Graphene Council and the nanotechnologies industry association as well as industry, standards bodies and other key players. Strong engagement and input into the project was received by these at the stakeholders advisory group meeting.

Early awareness and impact has been achieved via 16 presentations at international, european and national conferences and workshops. Consortium members are very active in key standardisation committees including ISO TC229. Members have participated in 20 meetings, this includes general participation, presentation of the project, and leading the development of new standards.

A website has been created which as well as general information about the project also has a news section which is being regularly updated with news stories from the project. The consortium also has Twitter and Linkedin accounts, consortium members also post updates of the project on Linkedin using their own accounts. The first publication highlighting the publication of the first graphene measurement standard (ISO TS21356-1 led by the consortium) has been published in Nature review physics. A second publication on Raman spectroscopy of graphene has also been published.

Impact on industrial and other user communities

There are currently over 100 commercial ‘graphene’ producers worldwide, including leading graphene producers in Europe, with an 'on paper' offering of materials with vastly different properties and types. However, many suppliers (and buyers) are hindered due to uncharacterised material that can be more often graphite rather than graphene or have batch to batch variations. With this project and the resultant standards, the entire supply chain of graphene from manufacturers to application builders and final consumer will profit from clear material specifications and globally accepted characterisation standards. The suppliers will see a stable demand for their high value high quality products.

Application builders will profit from reliable and traceable materials supply as well as comparability and traceability of various parameters to metrological standards. This will further enhance the development of advanced graphene applications and will ultimately profit ordinary consumers with greater choices of technology as well as reliable functionality do to well-specified materials used in the products. The impact is therefore on the entire supply chain and it does not depend on the graphene price or application hype in the market.

Once the material itself is characterised reproducibly and in a way that allows cross-comparison, real-world products can be tailored and improved using specific types of graphene and related 2D materials. These products include those in solar cell and battery production, composites and coatings, aerospace and automotive products (who need strong light-weight components), along with advanced clothing and consumer products. Transparent and consensus driven metrology of graphene will enable companies that are producing

and using graphene in these and other future applications to have a clear and sustainable business, reliable products and a safer environment.

Impact on the metrology and scientific communities

Based on the projects results, validated methods for characterising the structural and chemical properties of graphene using SEM, AFM, XPS and Raman spectroscopy will be made available to the metrology and scientific communities via peer-reviewed publications and European and international standards. This will create a large impact on measurement and test laboratories who will be able to measure the increasing number of materials being produced by companies worldwide to an accredited standard. In addition, academics will be able to better reproduce scientific results, assess the applicability of results to different technology areas under investigation and understand how the material properties affect the performance of lab-scale products for different application areas.

The uncertainties for measuring the properties of graphene such as flake size, chemical composition, thickness, number of layers, etc is up to 50 % currently and will reduce typically by at least a factor of two as detailed below. The metrology and scientific communities will have the opportunity to take part in the international interlaboratory studies enabling them to benchmark themselves against peers, along with a chance to improve their abilities to measure graphene more accurately. On a broader scope, the project will strengthen the collaboration of European NMIs in the area of nanomaterials and will increase their competitiveness and consistency in graphene characterisation in a competitive international market.

Impact on relevant standards

Standards cannot be developed without proven and verified methodology. Normative documentary standards are based on methods or procedures developed through interlaboratory studies and verified internationally. Before the project commenced there were no graphene standards available beyond terminology and an overview technical report, neither of which contains such verified methodology. This project is targeting the current gaps by leading four international interlaboratory studies and leading the development of three international standards in ISO TC229 and IEC TC113. This project will directly lead to the faster publication of these standards internationally and as European standards via CEN TC352. To this end, the first graphene measurement standard ISO TS 21356-1 on structural characterization of graphene has been published in March 2021 led by the consortium.

Longer-term economic, social and environmental impacts

Standards in general, but graphene standards in particular, aim to provide a level-playing field for the graphene industry where the main beneficiary is the customer – the innovative product developer and the final consumer. Without clear standards and accepted specifications, it is impossible to develop such a sustainable supply chain. Some previous nanomaterials have bypassed specification developments with companies arguing their unique properties and have subsequently found low acceptance and application of their “wonder material” by the global market. Without this project, these standards will take substantially longer to publish and will have a larger amount of informative content, both of which will hamper industry and lead to the possibility that companies will have developed different internal processes. This will mean a substantial amount of time and investment will be wasted and require further effort to rectify. As most companies in this industry are SMEs, this may mean otherwise very profitable companies will struggle to survive financially. This would be a substantial loss to the market overall and hamper advances in technology.

Many industries that use graphene including flexible electric/photonics, solar cells, and various medical, chemical and industrial processes will benefit from the well characterised graphene that will be able to be obtained as a result of this project. The purchasers of graphene will also benefit from the confidence of being able to purchase graphene with known properties and less batch to batch variability. Without overcoming this metrological barrier, the potential of this disruptive material will not be truly realised and thus advancements in many important grand challenges, such as aging population, the internet of things, light-weighting, and improvements in energy storage, will be slower.

List of Publications

1. Clifford, C.A., Martins Ferreira, E.H., Fujimoto, T. et al. The importance of international standards for the graphene community. Nat Rev Phys 3, 233–235 (2021). https://doi.org/10.1038/s42254-021-00278-6

2. Sacco A.,Portesi C.,Giovannozzi A.M., Rossi A.M. Graphene edge method for three-dimensional probing of Raman microscopes focal volumes. Journal of Raman Spectroscopy 52(10) 1671-1684 (2021) https://doi.org/10.1002/jrs.6187

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:		01 September 2020, 36 months
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Chief Stakeholder Organisation: ISO TC229 / JWG2		Chief Stakeholder Contact: Naoyuki Taketoshi
Internal Funded Partners: 1. NPL, United Kingdom 2. BAM, Germany 3. INRIM, Italy 4. LNE, France	External Funded Partners: 5. BREC, United Kingdom 6. CNRS, France 7. HAY, United Kingdom 8. IMDEA, Spain 9. KIT, Germany 10. UoM, United Kingdom	
RMG: -		