Publishable Summary for 17SIP03 ESCoShell
An ISO Technical Report on the use of Electron Spectroscopy for Measurement of Core-Shell Nanoparticle Shell Thicknesses

Overview

The aim of the project was to produce an ISO Technical Report on measurement of coating thicknesses (often referred to as the 'shell' thickness) on nanoparticles using electron spectroscopies such as X-ray spectroscopy (XPS) and Auger spectroscopy (AES). This has helped maximise the outputs of the EMRP BioSurf project which established the underlying metrology of key aspects of nanoparticle coating characterisation. The project has developed the ISO Technical Report and brought this to publication through ISO/TC 201 in 2021. This provides the user community with much needed validated methodology for measurement of nanoparticle coating thickness, increasingly needed in the fields of medical diagnostics, catalysis and optoelectronics.

Need

The Primary Supporter of this project, ISO/TC 201/SG1, "Nano-materials characterisation", represented by Don Baer (Pacific Northwest National Laboratory, USA) requested that the underlying metrology developed in HLT04 BioSurf on the measurement of nanoparticle coatings be conveyed into an ISO New Work Item to meet industry needs for progress towards standardisation of core-shell nanoparticle characterisation.

Coated nanoparticles are increasingly used in a wide variety of industries including medical diagnostics, catalysis and optoelectronics such as photovoltaic devices. In any application, knowledge of the thickness and surface chemistry of a nanoparticle coating is extremely important in understanding its behaviour and interactions with their environment. The capability to perform such measurements can be provided by electron spectroscopy. The ability to reproducibly and accurately characterise such nanoparticles is thus vital for the eventual development of nanoparticle systems for use in commercial applications. The ISO Technical Report produced by this project aids in the quick dissemination of protocols for sample preparation and analysis developed under HLT04 BioSurf, allowing for reproducible analysis of nanoparticle systems between instruments and laboratories.

Objectives

The objective of the project was to maximise the impact of BioSurf, specifically:

1. To publish an ISO Technical Report in ISO TC201 on methods for determination of nanoparticle coating thicknesses using electron spectroscopies.
2. To ensure the relevant user communities are aware of the ISO Technical Report and how it can improve the validity of their measurements and the development of their products.

Results

1. *To publish an ISO Technical Report in ISO TC201 on methods for determination of nanoparticle coating thicknesses using electron spectroscopies*

The aim was the publication of an ISO Technical Report under ISO TC201 (Surface chemical analysis) on the use of electron spectroscopies for measurement of nanoparticle coating thicknesses. It covers a variety of methods and concerns around the measurement of nanoparticle coatings using electron spectroscopy and helps to ensure that nanoparticle characterisation can be performed accurately and consistently between different analysts and instruments, providing users with confidence in the validity of their measurements. The effects of a range of variant nanoparticle structures, polydispersity, and composition on the interpretation of electron spectroscopy data are described. An initial draft was written with input from expert stakeholders. The document along with ballot papers was submitted and approved as a New Work Item via a Committee Internal ballot in ISO TC201. The document had strong support with 8 member bodies voting positively, along with 10 pages of comments. The document was thus approved as a draft technical report. The comments were used to update the draft which then underwent iterative revisions with the ISO experts. The document was then

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sent for draft technical report ballot which ran from 6 July to 6 September 2020 and was approved for publication with comments. These comments were used to further improve the document and the corrections checked with the experts. The document was then sent to BSI for editorial and figure checking. BSI edited some of the figures putting them into ISO format. The documents and figures were sent to ISO for publication. Due to various administrative and technical issues it took some time for ISO to accept these files and then subsequently process, edit and proof the documents. The proofs were produced and checked by NPL. The ISO technical report was published by ISO in June 2021, and can be accessed via ISO online: https://www.iso.org/standard/74821.html.

2. *To ensure the relevant user communities are aware of the ISO Technical Report and how it can improve the validity of their measurements and the development of their products.*

NPL and BAM disseminated the information on the development of the ISO Technical Report to the community as widely as possible. This was done by giving presentations at national, European, and international conferences in surface analysis to maximise awareness amongst nanoparticle and electron spectroscopy analysts. In total 15 presentations were given at conferences and workshops including 6 invited oral presentations which were presented in conferences in Europe, United states, Mexico, Japan and Korea.

Two publications have been published, one on "Determining the thickness and completeness of the shell of polymer core-shell nanoparticles by XPS, SIMS and T-SEM" and the other entitled "Determining nonuniformities of core-shell nanoparticle coatings by analysis of the inelastic background of X-ray photoelectron spectroscopy survey spectra".

In addition, in conjunction with the publication of the ISO Technical Report, NPL and BAM have submitted a summary version of the standard as a peer reviewed paper in the journal Surface and Interface Analysis. This was submitted in June 2021 and has been accepted for publication and so will be published in due course. In addition, NPL have published a short summary and publicity information summary *via* social media (i.e. LinkedIn), which has attracted over 950 views, in order to increase awareness and uptake by industry.

Impact

Nanoparticles are being increasingly used in a wider variety of commercial applications including consumer healthcare, drug delivery, coatings, electronics and catalysis. These nanoparticles are becoming increasingly more complex and intentionally designed with specific characteristics. Thus, accurate and valid characterisation of nanoparticles is increasingly important with a broad array of both academic and industrial laboratories engaging in or specialising in the analysis of nanoparticulate samples.

The outcome of this project was an ISO Technical Report under the auspices of ISO/TC 201 that provides clear and comprehensive methods and best practice for the measurement of nanoparticle coating thicknesses using electron spectroscopy techniques. It creates further impact from the results of the EMRP HLT04 BioSurf project which established the underlying metrology of key aspects of nanoparticle coating characterisation. The technical report also provides guidance and validated methods, which streamline the ability of industry to bring effective nanoparticle-based products to market. The engagement with the members of ISO/TC 201 has increased the impact of these efforts and driven progression towards standardisation. This committee has a strong industrial focus and is the global leader in surface chemical analysis standardisation with international experts respected throughout the scientific community. Industrial participants include Kratos Analytical (UK), SPECS (Germany), Tascon GmbH (Germany), ThermoFisher Scientific (UK), the British Standards Institute (UK), the German Institute for Standardization DIN e. V., AWE (UK), and several other major international companies.

Wider economic impact - Nanoparticles are currently used in an extremely broad array of industries, with applications in fields including catalysis, composite materials, medical devices, diagnostics, and drug delivery, opto-electronics, and many others. The use of nanoparticles in medicine and pharmaceuticals is a large and rapidly growing industry. In the field of drug delivery alone, the total market size for nanoparticle/nanocarrier based technologies is expected to surpass $130 billion (USD) over the next 5 years. By providing validated methods for measurement of such coatings and progress towards standardisation of these kinds of measurement, the ISO Technical Report greatly facilitates the development of such products and helps to meet regulatory requirements.

Nanoparticles also have great potential application as catalysts for a variety of purposes. With an expected global worth of over $30 billion (USD) for the catalyst market within the next ten years the development of coated nanoparticle-based catalysts has a significant potential impact.

Wider social impact - The ISO Technical Report impacts on the broader quality of life through the utilisation of coated nanoparticles in the healthcare and medical industries, as well as some potential use in consumer goods, such as sun cream. As previously mentioned, coated nanoparticles for use in medical applications are a large and growing industry and are likely to significantly impact on early diagnostics and treatment outcomes for major illnesses such as cancer and viruses.

Wider environmental impact - This ISO Technical Report aids in the development of several nanoparticle-based technologies which may have direct environmental impact, such as for oil recovery and in the field of photovoltaics and lighting and display technologies. The published ISO Technical Report will thus have use in a variety of nanoparticle applications in energy-related markets, leading to significant positive environmental impact.

Initial consultations with commercial XPS service providers and academics suggested that there will be a good uptake of this technical report for the determination of nanoparticle coating thickness and chemistry. Publicity of the development of this ISO document has been undertaken via social media and a submitted peer-reviewed publication. The document was discussed in 2018,2019 and 2020 at the annual meetings of the *ISO TC* 201 plenary and sub-committee meetings. Here, in each year the experts were informed about progress of the technical report and input received. Experts included NMIs, instrument vendors, measurement service providers and industry stakeholders. During the project, 15 presentations on the project were made at national, European, and international conferences. This includes six invited talks.

In conclusion, the main impact of this project is the usage of this ISO technical report, which will become a reference point for nanoparticle coating thickness and chemistry in order to aid products in key industrial sectors and accelerate innovation.

List of publications

- Determining the thickness and completeness of the shell of polymer core-shell nanoparticles by XPS, SIMS and T-SEM, The journal of Physical Chemistry C, *https://doi.org/10.1021/acs.jpcc.9b09258*
- Determining nonuniformities of core-shell nanoparticle coatings by analysis of the inelastic background of X-ray photoelectron spectroscopy survey spectra, Surface and Interface Analysis, *https://doi.org/10.1002/sia.6865*

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

Project start date and duration:	01 May 2018 and 36 months	
Coordinator: Charles Clifford, NPL Tel: 44 20 8943 6620 E-mail: charles.clifford@npl.co.uk Project website address: N/A		
Primary Supporter: ISO TC201/SG1 c/o Pacific Northwest National Laboratory, USA, represented by Dr Don Baer, chair		
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