Publishable Summary for 14IND12 Innanopart
Metrology for innovative nanoparticles

Overview

Nanoparticles are increasingly used in innovative products manufactured by advanced industries and provide enhanced, unique properties of great commercial and societal value. The demand for high performance materials places increasingly stringent tolerances on the properties of nanoparticles. The Innanopart project focusses on the major unmet metrological needs in the production of high quality nanomaterials: measuring the concentration of particles and measuring the surface chemistry. These two measurements are critical to the performance of these novel materials in products and the development of valid measurement approaches, supported by documentary standards, will underpin trade and the supply chain for these novel products.

Need

Europe has a significant share of both the ~€3bn global production and use of high performance nanoparticles and nanoparticle-enabled products, which is dominated by polymeric, noble metal and quantum dot nanomaterials. It is therefore essential to establish the key measurement methods to support the manufacture, performance and reliability of such materials. Many types of innovative nanoparticles exist: metals used in catalysis, medical applications and conductive inks; metal oxides employed in fuel cells and ferrofluids and as contrast agents for magnetic resonance imaging; semiconductors used as quantum dots and rods for bioimaging, photonics, display and lighting technologies; and organic particles used for electronic applications, drug delivery vehicles, fluorescent reporters and advanced coatings.

Measuring the concentration of nanoparticles in suspension is required to optimise and reproduce formulations and products. In most cases, this number concentration is not known but is calculated upon the basis of assumptions and mass-balance considerations. Currently, there are a number of methods which may be capable of measuring nanoparticle number concentration in colloidal suspension, but no standards or primary methods exist and no certified reference materials are available. The linearity, sample dependence, uncertainty and comparability of methods has not been established, even for ideal materials, and no validated reference materials exist for the calibration of commonly used instruments.

The surface chemistry of particles determines their behaviour and performance. Any surface modification, whether intentional or not, needs to be measured to fully understand the particles and their behaviour. Hence, measuring the surface chemistry of particles and quantifying the number of functional groups available for further reaction is fundamental to the successful formulation of products and their reliable operation.

Objectives

The specific technical objectives of the project are to:

1. Develop traceable measurement and calibration protocols to measure particle number concentrations in liquid suspension with a target relative uncertainty of better than 10 % for spherical particles in the size range 1 nm to 1000 nm.
2. Develop methods to quantify the number concentration of particles in partially agglomerated or aggregated states within a liquid suspension of otherwise monodisperse primary particles and the ability to measure number concentration of particles with a non-spherical shape.
3. Develop standard procedures to traceably measure the chemical composition and thickness of the nanoparticle shell, both to within 10 % uncertainty.
4. Conduct two inter-laboratory studies to establish a good practice guide for industry and thereby establish laboratory-scale methods to enable valid, routine monitoring and quality control of particle concentration and surface chemistry for nanoparticle-based formulations and products.

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

5. Engage with industry that manufactures and or / exploits nanoparticles in order to facilitate the uptake of the technology and measurement infrastructure developed by the project, to support the development of new, innovative products, thereby enhancing the competitiveness of EU industry.

The project additionally includes an investigation of the effect of particle shape upon number concentration measurements for nanoparticles in a liquid suspension. The importance of non-spherical particles in innovative applications is growing and this additional activity addresses this emerging need.

The results of this project will provide input to existing standards and stimulate the creation of new international standards which will enable both the concentration and surface chemistry of particles to be measured in a consistent and comparable manner. The partners will disseminate the results to a range of technical committees and standards bodies (e.g. ISO/TC 229, ISO/TC 201, ISO/TC 202, ISO/TC 24/SC 4).

Progress beyond the state of the art

Two independent routes for traceable measurements of particle number concentrations through SAXS (Small Angle X-ray Scattering) and spICPMS (single particle Inductively Coupled Plasma Mass Spectrometry) will be developed for monodisperse materials. The sensitivity, linearity, size and material dependence of laboratory techniques will be determined and a full uncertainty budget for all methods will be produced, together with calibration procedures for techniques used by industry. The particle number concentration will be determined with a target uncertainty better than 10 %. Additionally, we will investigate methods capable of resolving multimeric particle populations with particles agglomeration levels ranging from 0 % to 50 % and develop methods for measuring the fraction of particles in agglomerated states using DCS (Differential Centrifugal Sedimentation) and SAXS.

A quantitative framework that can rapidly and accurately measure both the shell thickness and its chemical composition will be developed using X-ray Photoelectron Spectroscopy (XPS). Methods to measure the concentration of surface functional groups on nanoparticles *in situ* will be developed using conductometric and potentiometric titration, as well as novel non-linear optical methods. The industrial relevant methods will be compared to accurate techniques like mass spectrometry, elemental analysis, NMR spectroscopy and XPS.

The results of VAMAS (Versailles Project on Advanced Materials and Standards) interlaboratory studies will codify the best practice for industry in these areas and initiate new work items and contribute to emerging documentary standards in ISO. This will result in the generation of reference materials suitable for assessing the ability of laboratories to measure number concentration and shell thickness of spherical nanoparticles.

Results

The project will establish reference materials, assess and compare the performance of different techniques, initiate pre-normalisation studies and provide input to internationally accepted standards.

Particle number concentration

The project has focused on producing spherical reference materials in the size range of 1nm to 1000nm which are being fully characterised and will be used later to calibrate laboratory instrumentation.

Further work has included the initial experimental set ups required for the accurate methods of SAXS and sp-ICPMS. Using some of the preliminary samples, the nebulisation efficiency of the sp-ICPMS instruments have been investigated and an improved SAXS set-up has been successfully implemented.

Non-spherical particles

Partners have made good progress on the production and initial characterisation of controlled agglomerates from Au and polymeric nanoparticles. Further work is ongoing to ensure that they are suitable for the intended purpose and have sufficient stability. In addition, DotRods (elongated, non-spherical quantum rods) have been purchased and characterised.

These agglomerate fraction and non-spherical test samples will be used to establish the sensitivity of laboratory methods to deviations from ideal, monodisperse, spherical particles. Protocols to determine the fraction of agglomerates in a suspension of monodisperse primary particles will be defined.

Chemical composition and thickness of the shell
Partners have developed core shell particles of varying shell thicknesses and preliminary FCS measurements have been carried out. These test materials will be used to develop accurate methods to measure the surface chemistry and thickness of surface coatings of particles.

Work is well underway to develop theoretical understanding of photoelectron emission from core shell particles using electron transport simulations. A paper has been published which evaluates the internal structure of core-shell nanoparticles using XPS intensities and simulated spectra.

Inter-laboratory studies and good practice guide
A VAMAS international inter-laboratory study on measuring shell thickness on particles using calibrated reference materials is near completion and will enable valid, routine monitoring and quality control of surface chemistry for nanoparticle-based formulations and products.

An additional VAMAS international study on inter-laboratory particle number concentration will also be initiated at a later stage in the project. Methods will be disseminated through a good practice guide, peer-reviewed papers, conferences, dedicated workshops and websites to ensure the widest possible benefit.

Engagement with industry
Partners are contributing to a number of international standard committees: ISO TC229 (Nanotechnologies), ISO TC201 (Surface Chemical Analysis), ISO TC202 (Microbeam Analysis) and ISO TC24 SC4 (Particle Characterisation). A new work item for ISO TC201 has been initiated "Surface chemical analysis - X-ray photoelectron spectroscopy - Calculating and reporting detection limits for elements in homogeneous materials"

A practical training course on DCS techniques, for measuring particle number concentration is under development and will take place later in the year, At a later stage (towards the end of the project) a dedicated and industry-focussed workshop for all new methods is planned and an e-learning tool will be developed.

Impact

Partners have already presented project results and progress on 8 separate occasions in European and international conferences. A paper has already been published and another is awaiting publication; in addition a chapter to a book on particle size distribution has also been approved for publication.

All these activities, in addition to the contributions to standardisation bodies (see results section above) will promote the uptake of methods. The project has a strong number of collaborators (13 to date, and more expected), who are interested in participating in inter-laboratory studies. The project also retains an interested group of stakeholders to ensure the needs of interested parties are fed into the project.

This project extends nanometrology beyond the well-established measurement of size to enable routine monitoring of particle number concentration and chemistry. These measurements represent major progress in supporting the production of reliable nanomaterials. Through these advances in measurement, nanomaterial suppliers and users can have confidence that batch-to-batch variability will be minimised and, by providing international standards for these measurements, world-wide trade in nanomaterials and European competitiveness will be enhanced.

Typically more than half of the nanoparticles produced for high performance applications fail to meet specifications. Numerous cycles of production and measurement are required to optimise processes and counteract this failure rate. The current cost of validating nanomaterials by electron microscopy is approximately € 2000 per sample; this could be reduced by an order of magnitude through the provision of guidance, standards and more cost effective methods as intended by this project. We envisage that these standards will strengthen and grow the current € 3 bn market in high performance nanoparticles.

The emerging nanomaterials industry in Europe is at a critical juncture. The EU is rightly seen as the most cautious and conservative market for nanotechnological products because of imminent regulation and reporting requirements. It is imperative, therefore, that the EU is seen to be leading the global community in providing measurements and standards in support of its legislative ambitions. The European Commission has challenged nanomaterials manufacturers to state the composition of their materials. Those industries that meet the challenge will improve their productivity and competitiveness because of their greater understanding of their own products and their ability to provide specifications to their suppliers. This project offers a coordinated effort to establish the measurement framework to support EU companies in the production of better, more competitive products, develop methods and instrumentation to measure nanoparticles and to meet EU regulatory requirements.

The project will contribute to an improved acceptance of nanotechnology and nanotechnology-based products by society through the dissemination of validated protocols for measurement of nanoparticle number concentration and surface chemistry. This will help to provide a reliable basis for the acceptance of nanoparticle-containing products by the consumer. Moreover, by improving the measurement of nanoparticles produced for innovative applications, this project will enable industry to finely control the production of nanoparticles so that more reliable, efficient and new products can be generated with higher performance. Specific output targets of this project are particles designed for the medical and electronic industries, which have substantial societal impact in terms of improving health and quality of life.

List of Publications

- Evaluating the Internal Structure of Core−Shell Nanoparticles Using X-ray Photoelectron Intensities and Simulated Spectra , M. Chudzicki, W. S. M. Werner, A. G. Shard, Y.-C. Wang, D. G. Castner, and C. J. Powell, J. Phys. Chem. C, 2015, 119 (31), pp 17687–17696

Project start date and duration:	01 May 2015 (36 months)	
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