

General guidance for the surface analysis of nanoparticles

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ABSTRACT

This document describes the requirements, important considerations, and appropriate methods for the analysis of nanoparticle samples by X-ray Photoelectron Spectroscopy (XPS). This includes discussion of: common types of nanoparticle sample and associated concerns; sample handling requirements and sample provenance; issues to consider when selecting an appropriate substrate and guidance on substrate cleaning; methods for mounting/deposition of a sample onto a substrate or sample holder and their associated advantages and disadvantages; analysis approaches available for determination of coating thicknesses on nanoparticles; and example protocols for the preparation of a samples using drop-casting and spin-coating methods.

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Approved on behalf of NPLML by
Andrew Pollard, Science Area Leader

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GLOSSARY/ABBREVIATIONS

AMRSF:	Average Matrix Relative Sensitivity Factor
DLS:	Dynamic Light Scattering
ISO:	International Organization for Standardization
LEIS:	Low-Energy Ion Scattering
PTFE:	Poly(TetraFluoroEthylene)
SEM:	Scanning Electron Microscopy
SESSA:	Simulation of Electron Spectra for Surface Analysis
SLA:	Straight Line Approximation
TC:	Technical Committee
TWA:	Technical Working Area
UHV:	Ultra-High Vacuum
VAMAS:	Versailles Project on Advanced Materials and Standards
XPS:	X-ray Photoelectron Spectroscopy

1 INTRODUCTION

The study of nanoparticles is a topic of great interest for both academia and industry, due to its potential applications across a broad range of fields, including optoelectronics¹⁻⁴, catalysis⁵⁻⁷, and pharmaceuticals and medicine⁸⁻¹¹. Due to the high surface area to volume ratio nanoparticles possess, the behaviour and interactions of nanoparticles with their environment are strongly influenced by their surface properties. For nanoparticles bearing a coating or shell, this surface dependence is even more emphasised, and the thickness and chemistry of a coating can be vital in determining the properties of a nanoparticle system. In reality, most nanoparticles possess some form of shell or coating either by intent to alter the nanoparticle's properties, or incidental such as layers of oxide, unintended adsorbates or contamination. Given the importance of nanoparticle surface properties, the use of surface analysis techniques is recommended to provide relevant measurements, particularly of the thickness and composition of nanoparticle coatings or shells.

Currently, the lack of adequate and complete characterisation of nanoparticle systems poses a major barrier to their use in practical application¹². This document will describe some of the fundamental requirements and issues involved in the study of nanoparticle samples using surface analysis techniques, with a particular focus on the use of X-ray photoelectron spectroscopy (XPS). Guidance for nanoparticle analysis is given, including: discussion of substrate choice and preparation for samples in liquid suspension; common deposition methods for samples from liquid suspension; common sample mounting methods for powders; analysis methods for determining nanoparticle coating thicknesses; and a case study of a VAMAS project on interlaboratory reproducibility of nanoparticle coating measurement.

There are ongoing standardisation activities on the topic of nanomaterial sample handling and surface analysis by bodies such as ISO TC201 – Surface Chemical Analysis. Where possible, analysts should consult the latest relevant publications from such bodies for guidance. In particular, handling and preparation of samples for surface analysis is covered extensively in ISO 20579, of which part 4 specifically pertains to nanomaterials¹³. Other recommended resources on the topic of nanomaterial surface analysis include: ISO/TR 14187 : ‘Surface chemical analysis -- Characterization of nanostructured materials’¹⁴; Chapter 8 (‘Surface Chemistry’) of the textbook ‘Nanomaterial Characterisation – An Introduction’¹⁵; ‘The Chameleon Effect: Characterization Challenges Due to the Variability of Nanoparticles and Their Surfaces’¹⁶; and the e-learning course ‘Measuring the Surface Chemistry of Nanoparticles using XPS’ on the NPL e-learning website¹⁷, which includes a spreadsheet for calculating overlayer thicknesses on both flat and nanoparticle samples using the method outlined in section 4.2.

2 REQUIREMENTS OF SURFACE ANALYSIS

Surface analysis techniques such as XPS typically have very stringent sample preparation requirements. As XPS typically provides information from the top <10 nm of the surface of a sample, very little contamination is needed before a clear effect on the measured spectra can be observed. Therefore, samples prepared for XPS must exhibit a high degree of cleanliness. Likewise, the sample itself should be isolated from other materials, particularly those which may contain the same elements. For example, for samples of synthetic materials which contain remnants of the precursors used in their production, it will prove difficult to obtain practical, quantitative information. As an ultra-high-vacuum (UHV) based technique, samples for XPS must also remain stable under such conditions. Similarly, samples must remain stable under irradiation by the x-ray source, or experiments must be conducted with the potential for such beam damage in mind (e.g. by minimising x-ray exposure, defocussing the x-ray monochromator, tracking changes in the sample with exposure time, etc.). In general, it is preferable for samples intended for XPS analysis to be conductive, in order to prevent charging effects, however many instruments are now equipped with charge neutralisation methods such as electron flood guns, so this requirement may be mitigated to a degree. For samples which require deposition onto a substrate prior to XPS analysis, appropriate substrate choice can also be important in mitigation of potential charging issues.

3 SAMPLE HANDLING AND PREPARATION

When performing surface analysis on nanoparticles, there are many issues from sample preparation to data analysis that must be taken into account in order to obtain accurate, representative data and interpret it appropriately. Many of these apply to surface analysis procedures in general, while several are specific to nanostructured systems or even specific types of nanoparticle. The following sections outline several common areas where difficulties may arise, and also appropriate practice for minimising sources of error.

3.1 SAMPLE HANDLING

As with any sample being prepared for surface analysis, great care must be taken to avoid sources of contamination. Any laboratory utensils and glassware used to handle the samples should be rigorously cleaned before and after use. Ideally glassware used for nanoparticle samples should be replaced on a regular basis to avoid potential long-term build-up of nanoparticle contamination within wear on older vessels. To minimise incidental contamination, powder-free disposable laboratory gloves should be worn when manipulating samples for surface analysis. Even while wearing gloves, direct handling of samples should be avoided whenever possible; manipulation should be carried out using clean tools that will not transfer material, such as metal laboratory tweezers, and contact with the surface for analysis avoided or minimised. If the use of solvents is required during sample preparation, care must be taken to avoid potential transfer of contaminants from gloves to the sample through the solvent¹⁸. To minimise exposure to atmospheric contaminants, sample containers should remain closed at all times when not in active use.

Health and safety concerns with nanoparticulate samples can vary significantly depending on the material, size, and format of the sample, and a comprehensive discussion is beyond the scope of this document. At a minimum, samples should always be handled while wearing full standard protective gear appropriate to a chemical laboratory, a full risk-assessment should be conducted before handling the material, especially if it is powder form, and all waste should be disposed of according to local guidance. Nanomaterial powders should always be handled in a fume hood with appropriate particle filters fitted.

3.2 SAMPLE PROPERTIES

When preparing nanoparticle samples for surface analysis, it is important to have as much information as possible regarding the properties of the specific sample provided. Often, the nanoparticles to be studied may not be the only material within the sample. For example, remnants of synthetic precursors, excess functionalisation molecules, or other previous chemical processing by-products may be present alongside the nanoparticles. The properties of the nanoparticles themselves may also have a significant impact upon the preparation procedure required. Specific conditions may be required to avoid sample degradation, e.g. by heating or cooling beyond certain temperatures, exposure to air, or contact with specific materials (Figure 1). The impacts of sample format and properties are therefore significant.

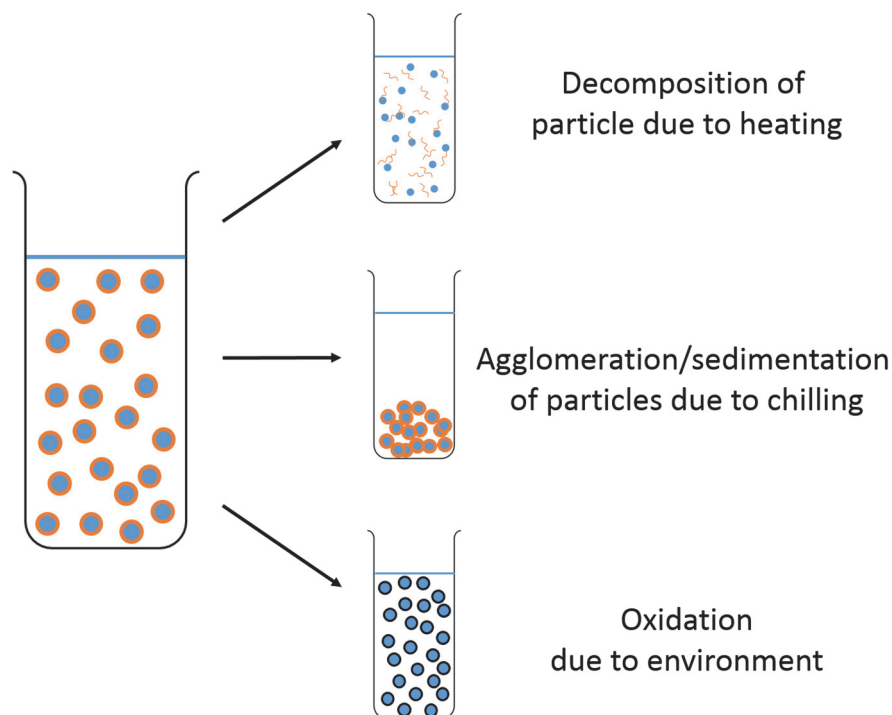


Figure 1 - Schematic of common nanoparticle sample degradation mechanisms

As with any sample prepared for XPS analysis, the presence of extraneous material is to be avoided wherever possible. For liquid suspensions of nanoparticles, non-volatile solutes may often be removed or 'cleaned' from the sample using methods such as dialysis, centrifugation, diafiltration, and various combinations of these methods^{19–22}. Each has advantages and disadvantages, and the specific nanoparticle sample and laboratory setup may have a significant influence on the choice. Centrifugation and dialysis are typically the most popular methods due to their accessibility²⁰.

Care must be taken in purification of nanoparticle samples, as this may lead to a risk of agglomeration or sedimentation due to the removal of stabilising agents in the solution²³. Many cleaning methods also carry an inherent risk of biasing the sample, particularly in the case of highly polydisperse samples, where particles at the extremes of the size distribution may be inadvertently 'cleaned' from the solution. Table 1 provides a summary of the most commonly used methods for cleaning nanoparticle suspensions, their requirements, limitations, and possible issues with their use.

Comparisons between centrifugation and dialysis for gold nanoparticles synthesised using the citrate reduction method found greater aggregation and remaining excess citrate when using dialysis²⁰. Centrifugation is therefore recommended as the first resort for removal of unwanted material from nanoparticle solutions.

Cleaning Method	Equipment required	Applicability	Possible issues
Centrifugation (recommended)	Centrifuge & appropriate vessels. Vessels with a low-bind coating to prevent adhesion may be necessary for some particles.	Ideal for large, dense particles. As particle density and size decreases, centrifugation becomes more time consuming. Cannot be used for particles of density close to or below the medium in which they are suspended.	Care must be taken to avoid loss of sample from aggregates crashing out of solution, or finer particles being removed with the supernatant.
Dialysis	Dialysis tubing with appropriate pore size – i.e. smaller than the smallest particles within the sample, and larger than expected contaminants	Can handle low-density samples, but effectiveness is reduced if contaminants are similar scale to particles	Many cycles may be required to achieve appropriate levels of cleanliness, loss/biasing of sample is also a concern.
Diafiltration	Several types of filtration system are available; it is key that filter size should be selected to not lose sample, while removing contaminants.	Can handle low-density samples, but effectiveness is reduced if contaminants are similar scale to particles	Some sample may be lost on the filtration medium, biasing of sample is also a concern.

Table 1 - Summary of cleaning methods for nanoparticle suspensions

A reasonable centrifugation-based cleaning protocol was utilised in the VAMAS TWA 2, Project A19 interlaboratory study on measurement of coating thickness on gold nanoparticles²². This consisted of three cycles of centrifugation, each followed by pipetting off excess liquid (without disturbing the concentrated pellet of nanoparticles) and re-dispersal of the nanoparticles in ultrapure water (see Figure 2).

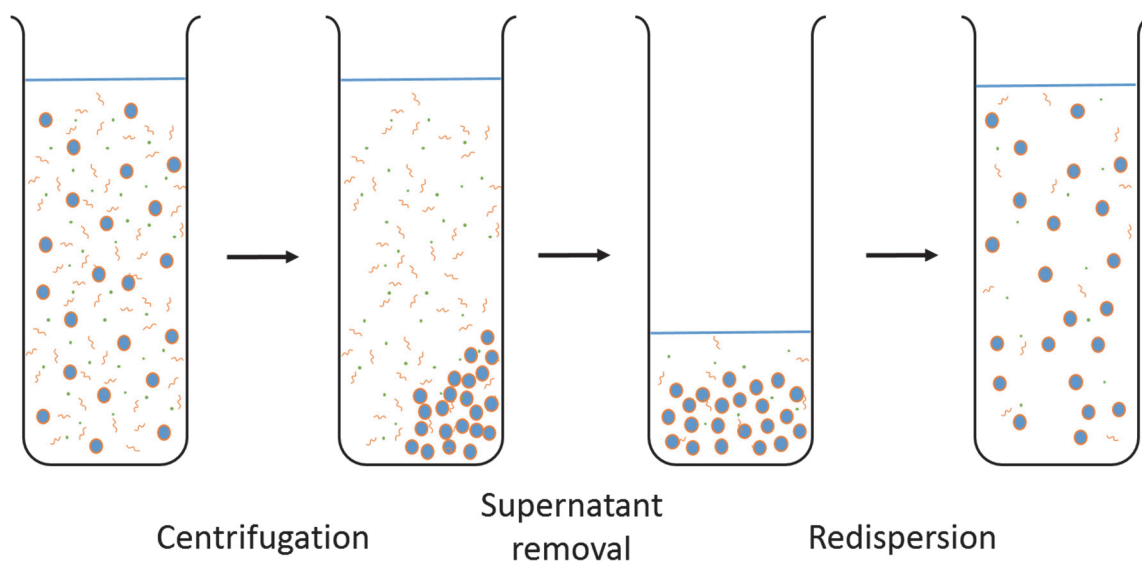


Figure 2 - Schematic of the process of removing unwanted material by centrifugation.

Maintaining the appropriate environment to avoid degradation of the nanoparticles is of course advisable. If unavoidable however, and where samples are intended solely for analysis using XPS, certain forms of sample degradation may be acceptable. For example, agglomeration, if known to not result in alteration of the structure or composition of the particles, will have little effect on measurements obtained using XPS. In general however it is recommended to avoid any unnecessary alteration of the sample.

3.3 PROVENANCE INFORMATION

It is of great importance, particularly when analysing nanostructured samples which may be highly susceptible to alteration, that as much as possible is known about the conditions and procedures a sample has experienced prior to surface analysis^{12,24}. Without such information, measurements may be misunderstood or difficult to interpret. It is recommended that a comprehensive record of sample provenance is kept for any nanoparticle sample. As a guideline, this should include information such as: synthesis method, materials used, and date of synthesis; storage information, including conditions of storage, vessel, duration, and details of any shipping or significant transport; details of any additional treatments or procedures applied to the sample, such as resuspension, heating and cooling, washing etc.; details and results of any prior analysis or characterisation performed on the sample, including information on any sample preparation procedure used and the date of analysis; and details of any other events or dates that may be important, such as the first opening of a sample container, extended open-air exposure, expected expiry date, etc. The ISO standard on the handling of nanomaterials and sample preparation for surface chemical analysis (ISO TS 20579-4¹³) states in greater detail the specific information that should be included in such a provenance record for nano-objects, with associated examples.

3.4 SUBSTRATE CHOICE

When preparing samples of nanoparticles in liquid suspension for surface analysis, the sample must first be deposited onto a substrate. There are several factors to consider in selecting the appropriate substrate for a given sample. The main concerns are outlined below, along with several examples of suitable substrates in common use.

3.4.1 Peak interference

It is extremely important that there be no material present which obscures or limits the analysis of the resulting data. Therefore it is recommended to avoid any substrates containing elements identical to those in the sample. Perhaps less obvious, but equally troublesome, is the presence of elements whose spectra contain peaks coincident with those of the sample. It is sometimes possible to use alternate peaks from an element, but in cases with samples that have few quantifiable peaks or substrate materials with many significant peaks analysis may still be hindered. If a specific substrate material is required, the effects of any peak interference may be minimised by ensuring as thick and uniform a deposit of nanoparticles as possible, in order to reduce the signal arising from the substrate. Some suggestions for substrates are given below at 3.4.4.

3.4.2 Surface wetting

When depositing particles from liquid suspension, the wettability of the liquid is a major concern for both sample and substrate. In general, minimal wetting of the substrate, i.e. a high liquid contact angle, is desirable for drop-casting of samples as discussed at 3.5.1 (as long as deposit area remains large enough for analysis), while greater wetting, i.e. a low liquid contact angle, is preferable for spin- or dip-coating as discussed at 3.5.2. If multiple deposition cycles are required, as is typically the case when drop-casting, it is helpful if the nanoparticles in the sample are more wetting than the substrate. If this is not the case, it can be extremely difficult to place multiple depositions on the same location, greatly decreasing the achievable thickness and uniformity of the deposit.

3.4.3 Contamination

Substrate contamination is a significant issue, particularly when analysing samples containing carbon. Almost all surfaces exhibit some degree of adventitious carbon contamination unless cleaned with extreme rigour and kept in a clean atmosphere until introduction to vacuum. For organic and other carbon-containing samples, this is a particular problem, as it can be difficult or impossible to separate the carbon signal due to substrate contamination from hydrocarbon present in the sample. For samples where this is the case, it is therefore imperative that substrate contamination be minimised either by cleaning of the substrate, or completely obscuring the substrate with sample material. A cleaning protocol, as used at NPL for silicon wafers, is presented in the appendix. Depending on the degree of cleanliness required and the cleaning methods available, it may be preferable to select a substrate less prone to contamination.

3.4.4 Commonly used substrates

The following is a small selection of commonly used substrates and their advantages/disadvantages.

- Silicon wafer is one of the most commonly used substrates for XPS, because it is readily available in high purity. Its surface can be cleaned easily, it is easily cut to appropriate sizes using a diamond scribe, and is relatively easy to use for drop-casting. If needed, UV-ozone treatment in the cleaning process can render the surface more hydrophilic, which can be particularly useful for spin-coating. Silicon wafer is of course unsuitable for use with silicon-containing samples, and inadvisable if quantification of oxygen is required; the layer of silicon dioxide typically found on the surface of a wafer can be difficult to isolate from oxygen in the sample due to the narrow range of chemical shifts for different oxygen 1s peaks.
- Gold coated silicon wafer shares many of the advantages of silicon wafer, with the additional benefit of lacking any intrinsic oxygen or silicon. It is therefore suitable as a replacement for silicon wafer when investigating samples containing these elements. It does however have a significant disadvantage in that the gold spectrum is highly intense, and contains several peaks at a range of binding energies. This results in a much higher chance of overlap with sample peaks. The intensity of the gold spectrum may sometimes prove useful as a means of identifying

the thickest regions of a deposited sample: as the gold 4f peak is reduced or removed, it can be assumed that there is minimal signal arising from contamination on the substrate.

- Poly(tetrafluoroethylene) (PTFE), either as solid sheet or tape wrapped around a suitable mount, can be a useful substrate for XPS. It benefits from a typically very low level of adventitious carbon contamination and a naturally high degree of hydrophobicity, rendering it ideal for drop-casting. The XPS spectrum of fluorine presents little chance of overlapping with peaks from most samples, and the carbon present in the substrate can be easily isolated from the majority of carbon-containing samples due to the high chemical shift of the C 1s peak for carbon bonded to fluorine. More complex carbon spectra, particularly those containing high-binding-energy species, may prove more difficult to dissociate from the substrate. Due to its highly hydrophobic nature, PTFE is also unsuitable for spin- or dip-coating.
- For powder samples, malleable tapes or metal foils are often used as a substrate, as described in section 3.5.3. Indium foil is the most commonly used for this purpose²⁵, however this may be disadvantageous for some materials due to its spectrum containing many peaks, increasing the likelihood of peak interference. PTFE tape may also be used for some materials, with due consideration of its properties as noted previously.

Other common substrates that may be used, whether for their suitability to a particular characterisation technique, relevance to real-world applications, or otherwise, include: indium-tin-oxide coated glass (ITO); highly-ordered pyrolytic graphite (HOPG); copper TEM grids; and molybdenum or tantalum foils

3.5 DEPOSITION/MOUNTING METHOD

Several methods are available for the deposition of liquid suspensions of particles onto a substrate. Several of the most commonly available options are described below, with guidance on effective implementation. Likewise, for dry powder samples, multiple methods of sample mounting exist, and are briefly discussed at the end of this section. A summary of the methods discussed in this section is provided in Table 2.

For samples formed by deposition from liquid suspension, it is recommended to inspect the deposit before analysis to ensure a reasonable level of uniformity in coverage has been achieved. For many samples this may be reasonably judged by eye, however for many, particularly those that are pale, translucent, or similar in hue to the substrate, it may be advisable to use optical microscopy or, if feasible, scanning electron microscopy (SEM) of a sample prepared identically to the sample prepared for XPS analysis. SEM of the actual sample to be used for XPS is not advised due to the potential for modification of the surface. Even with such measures it can be difficult to guarantee a uniform and thick deposit has been achieved, and so analysts should always be prepared to observe the presence of the substrate when performing analysis. If the guidance above on substrate choice has been followed however, the impact of this may be minimised.

Method	Ease of Use	Advantages	Disadvantages
Liquid: Drop-casting	Straightforward but time-consuming	Applicable to the vast majority of samples, capable of producing high-quality depositions with minimal equipment or expertise required	Potentially extremely time-consuming. Optimisation of deposition protocol must be done on a sample-by-sample basis, as the uniformity of deposition can be highly sample dependent
Liquid: Spin-coating	Reasonably straightforward, requires spin-coating apparatus	Extremely fast, capable of producing highly-uniform films of nanoparticles	Requires samples to be in high concentration. Efficacy depends strongly on interactions between the sample and the substrate. May require trial and error to determine a suitable protocol for a given sample.
Powder: Pelleting	Straightforward, requires pellet press	Under optimal conditions produces an easily-handled solid pellet. Relatively quick to perform	Many samples may not form cohesive pellets upon pressing, and may be prone to falling apart
Powder: Tape or foil pressing	Straightforward	Quick and easy to perform	May be difficult or impossible to avoid signal from the substrate
Powder: Use of specialised holder	Requires powder container suited to the sample-entry system used.	Easy to use, minimal risk of undesired signal	Powder present is looser than other mounting methods, may be more mobile once within instrument. Sample may not be tilted.

Table 2 - Summary of deposition methods for nanoparticle suspensions and powders

3.5.1 Drop-casting

One of the most readily accessible methods of deposition for liquid suspensions of nanoparticles is that of drop-casting. Despite the simplicity of this method, if carried out with proper care it may produce extremely uniform, thick films of nanoparticles suitable for surface analysis. In order to drop-cast a sample, it is recommended to use a substrate which is relatively non-wetting to prevent excessive spreading of the droplet. For some substrates, this may mean that a superior deposition is best achieved by omitting any cleaning step that may result in a more hydrophilic surface (such as use of aggressive oxidising agents, UV-ozone treatment etc.) to ensure a thick deposit can be achieved.

Ideally a (grease-free) vacuum desiccator should be used to dry droplets between repeated deposition cycles, as otherwise deposition may take an excessive amount of time, during which the sample is exposed to contamination to a much greater degree. If a vacuum desiccator cannot be used, gentle heating of the substrate may be used to aid the drying process, however this should only be performed if absolutely certain that the heating will have no adverse effect upon the sample itself.

One of the main issues with this deposition method is the chance of developing ‘coffee-ring’ deposition²⁶, whereby the majority of the particles are deposited at the outer edge of the droplet as shown in Figure 3. In order to minimise this coffee-ring effect, and to improve the uniformity of the deposition in general, several measures may be taken:

- Sample concentration may be decreased, and the number of deposition cycles increased
- Deposition volume may be reduced between depositions, in order to produce a smaller ring each time. Some mixing of these ‘deposition rings’ is expected with each cycle, and ideally should result in a flatter distribution.

- A clean Viton O-ring may be placed around the deposition area (note: the drop should not contact the O-ring) in order to provide both a visual guide for droplet placement, and potentially limit evaporation from the edges of the droplet. (See section 7.2 for an example)

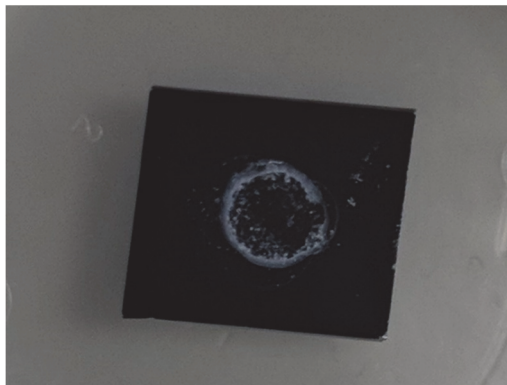


Figure 3 - An uneven deposition using the drop-casting method, exhibiting a strong-coffee ring effect.

In cases where the sample itself is highly hydrophobic, it may prove difficult to place droplets on top of existing deposition. In this case, it is recommended to either use a more hydrophobic substrate such as PTFE, reduce the volume deposited for consecutive deposition cycles to avoid contact with the substrate outside the deposition area, and/or reduce the number of deposition cycles (e.g. by increasing the sample concentration). If all of these methods fail, it is advisable to instead try a deposition method that is suitable for single deposition cycles, such as spin-coating.

The drop-casting deposition protocol provided to participants of the VAMAS interlaboratory study on the measurement of chemistry and thickness of nanoparticle coating thickness²² is provided at 6.2 in the appendix. An NPL-deposited sample is shown in Figure 4, showing that good depositions can be readily achieved with this method if the appropriate protocol is identified.

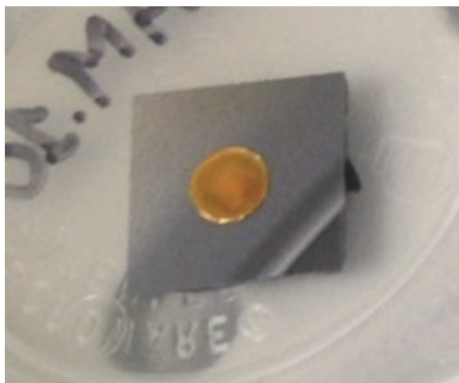


Figure 4 - A good drop-cast deposit of peptide-coated gold nanoparticles on silicon wafer, as sent to participants of a VAMAS interlaboratory study²².

3.5.2 Spin-coating

Spin coating can be an effective means of depositing nanoparticle films onto a substrate. Spin-coating typically allows rapid deposition of films, and has the potential to provide fine control over the thickness of the resulting film. This renders it ideal for samples of non-conducting material for which charging is expected during XPS analysis, as the film can be controlled to be as thin as possible without exposing the substrate. However there is a loss of versatility compared to drop casting, as samples for spin-coating are required to be high concentration – repeated cycles are unlikely to be possible without removing previous depositions. It is also inefficient compared to drop casting, as much of the droplet is spun off

the edge of the substrate and lost during the process. Unless an appropriate protocol for spin-coating a given sample is known in advance, determining the appropriate protocol may require trial and error, which can be difficult if the amount of sample available is low.

Substrates prepared for spin-coating should ideally be relatively hydrophilic – UV-ozone treated silicon wafer forms a highly suitable surface for this purpose. Hydrophobic substrates such as PTFE may prove difficult to spin-coat. Due to the spin-coating requiring only one deposition cycle, it is well suited to samples for which repeated deposition is awkward or difficult, such as those that are highly hydrophobic. Figure 5 shows an SEM micrograph of a film polymer nanoparticles that were deposited using a spin-coater. XPS from this film exhibited minimal charging and no visible substrate signal, whereas drop-casting of the same nanoparticles could not achieve a substrate-free spectrum due to the hydrophobic nature of the sample deposits, and strong coffee-ring effect (See Figure 3).

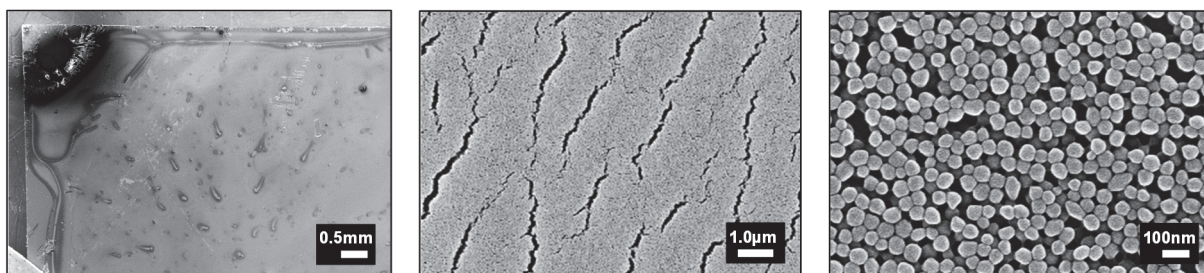


Figure 5 - SEM micrographs of a spin-coated deposit of polymer core-shell nanoparticles. The protocol used to produce this deposition is given in the appendix at 6.3.

3.5.3 Powders

For powdered samples there are a range of possible sample mounting options available, and typically there is little to separate the mounting of nanoparticle powders to that of larger grain sizes. Broadly considered, four common options exist for the mounting of powdered samples:

- Use of a specialised sample holder to contain the powder
- Use of a pellet press to form a solid pellet of the sample
- Use of adhesive tape to which the powder is stuck
- Use of malleable tape, into which the powder is compressed

Each of these options is viable for nanoparticulate powders, but depending on powder consistency and analysis requirements, one or another may prove superior.

Where available, the use of a specialised sample holder is an excellent option for mounting of powders. Figure 6 shows a type of sample holder custom made to fit the sample bars used at NPL, containing a nanoparticulate powder. Mounting powders in such a holder is relatively simple, and requires only to place the powder within, and compress slightly using a clean metal rod of the appropriate diameter. For powders that are particularly incompressible, trapped air within the sample can lead to scattering of the sample in the chamber during the pump down to UHV. If this is a concern, it is recommended to use a vacuum desiccator to test the sample under vacuum exposure before introduction to any instrument, to avoid contamination or damage.

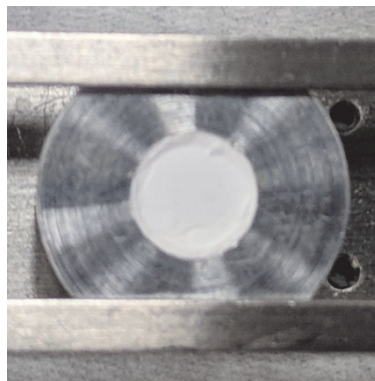


Figure 6 - Example of a sample inside a specialised powder sample container.

The use of a pellet press to form a solid pellet of a powdered sample can be highly effective, and allows the sample to be mounted much as many other solid samples would be. However many powders may not easily form pellets, or will only form fragile or crumbly pellets when compressed. While sometimes additives can be combined with a powdered sample to improve the quality of a produced pellet, this has little benefit over other methods, as it will guarantee the presence of undesired peaks within the XPS spectrum.

The use of double-sided adhesive tape provides a quick and facile method of powder sample mounting, and vacuum-stable adhesive tapes, typically carbon or copper based, are commonly found in laboratories containing UHV instruments. Tape should be placed over the powder and pressed from the rear, then removed. Excess powder should be shaken off, and all waste disposed of appropriately. It is best to avoid pressing the powder directly onto the tape with an implement such as a spatula, as these may leave metal residues which can be observed in the XPS analysis. Ideally a deposition in this manner should leave no exposed tape, however this may depend strongly upon the sample itself, and the use of adhesives introduces the question of contamination.

Malleable tapes or foils are commonly used as a mounting mechanism for powder samples undergoing XPS analysis, with Indium or other soft foils typically recommended²⁵. In order to mount a sample, it must be pressed between either two pieces of the mounting material, or between the mounting material and a clean, harder surface that may be disposed of afterwards. This method suffers from some of the same issues as the use of adhesive tape, in that any exposed substrate will be observed (along with any contamination on the surface) in the XPS spectrum. However, the lack of adhesive provides an advantage by potentially minimising the contribution to the XPS spectrum to a single material. PTFE tape may also be used in this manner, due to its softness and absence of surface contamination.

4 ANALYSIS

Typically XPS is used on bulk materials in order to determine the relative composition of elements (with the exception of hydrogen) and their different chemical states present within the surface of the sample. This is usually done assuming that all signal arises from a uniform homogeneous surface, and is reported as atomic percentage. For nanostructured samples these assumptions are incorrect, however those nominal atomic percentages can be corrected to gain valid information on overlayer thickness and composition. Using XPS, several methods exist for the measurement of the thickness of nanoparticle shells, and there is ongoing activity within standardisation bodies such as ISO TC201 concerning such measurements.

Three common methods for the calculation of nanoparticle shell thicknesses from XPS intensities are discussed below. Table 3 provides a summary of these methods, their advantages and disadvantages. Comparisons of the three methods have generally found them to provide good agreement, with the greatest deviation occurring for systems with thick, highly-scattering shells. In such cases, the inaccuracy arising from the straight-line-trajectory approximation (used for simple numerical modelling and empirical formulae) is more significant²⁷.

For all methods, it is either useful or necessary to know the core or total size of the particle in order to determine the shell thickness. Moderate polydispersity in core size does not have a significant effect on the obtained values, so an estimate of the average size from a supporting characterisation technique is reasonable. The effect of variation in core size becomes more significant as size decreases, and greater care should be taken to ensure a representative value is used for particles with core size approaching ~10 nm or smaller. Polydispersity in shell thickness will have a much more significant effect, and any calculation that does not take this into account will result in an underestimate of the shell thickness.

Where possible, for all methods it is recommended to measure reference intensities from bulk samples of the materials present in the sample, preferably during the same set of measurements as the samples themselves. By using the ratio of the measured intensity to the measured pure material intensity, this can help to mitigate any error arising from instrument transmission and relative sensitivity factors used.

Method	Advantages	Disadvantages
Numerical Modelling	Can be used to model XPS intensities for nanoparticles of a broad range of possible shapes/geometries.	Requires rudimentary scripting, and an understanding of the calculations and assumptions involved. Requires iteration to match intensities to observed values. If using the straight-line-trajectory approximation, may be inaccurate for systems with significant elastic scattering of electrons.
T_{NP} Formula	Simple to use, requiring no specialist knowledge	May be inaccurate for systems with significant elastic scattering, due to straight-line-trajectory approximation.
SESSA	Strong theoretical backing, accounts for all reasonable physical parameters; capable of modelling a broad range of topographies.	Requires purchase, and operates by iteration of a model to obtain a match to observed intensities.

Table 3 - Summary of methods for nanoparticle coating thickness calculation

4.1 NUMERICAL MODELLING USING STRAIGHT-LINE-TRAJECTORY APPROXIMATION

To determine the shell thickness and potentially other structural aspects of a nanoparticle system it is necessary to model the spectra from geometrical considerations. The most convenient and simple approach is to assume that electrons travel directly from the emitting atom to the detector – this is known as the Straight Line Approximation (SLA). Several examples of the use of numerical modelling using the straight-line approximation can be found in the literature, either for the development of models such as the T_{NP} ^{28,29} formula, as methods for direct modelling of specific systems³⁰, or as comparisons between various methods.

In general, this method involves writing a simple script or program for calculating XPS intensities from an infinitesimally thin slice or column of material³⁰. By careful consideration of the geometry of a given system, this is then repeated and intensities summed across the entire ‘top-down’ area of a nanoparticle to produce expected intensity ratios between each of the constituent elements. An example script, usable in MATLAB, performing this calculation for core-shell-shell particles is given in the supplementary information of Cant *et al.*²⁸.

This method has the advantage of being able to provide estimates of intensity ratios for monodisperse particles of arbitrary geometry. It can feasibly be applied to any nanoparticle system for which the XPS signal arising from a population of randomly oriented nanoparticles can be approximated to that of a

single particle. When using this method, care must be taken that all relevant factors in determining the intensities are correctly accounted for. The simplest method to ensure comparability of numerically calculated intensity ratios with experimentally measured values is by normalisation to measured pure-material intensities.

While this method is versatile, the user must also be aware that when using this to resolve nanoparticle structures, multiple unknowns could lead to more than one solution. For example, with no reasonable measure of a core or total diameter for the particle, multiple ‘solutions’ may exist that result in a match to the experimentally observed intensity ratios, but with different combinations of core radius and shell thickness. It is recommended to use this method when some information is known or can be estimated regarding at least one dimension of the nanoparticle. Due to the use of the straight-line approximation, which does not account for elastic scattering, the error in measurements made using this method will be increased for systems in which strong elastic scattering is expected, such as heavy elements.

4.2 T_{NP} METHOD FOR SPHERICAL CORE-SHELL PARTICLES

The T_{NP} formula for calculation of nanoparticle shell thicknesses is the most accessible and easy-to-use method for determining the thickness of a nanoparticle coating or shell. Developed at NPL as an empirical formula to estimate shell thicknesses from XPS data, it is based on comparison to numerical modelling using the straight-line approximation. In order to use the T_{NP} formulae to estimate shell thickness, the user requires an estimate of the core (or total) radius of the nanoparticle and the measured XPS intensities from a sample. Where possible, measurement of reference intensities from pure, bulk samples of the materials present in the nanoparticle may be used to improve the accuracy of this method. Once these have been obtained, application of the formula provides the user with a direct estimate of the shell thickness of the nanoparticle. A comprehensive explanation of the use and development of the T_{NP} method can be found in the original work by Shard²⁹. The formulae used in the T_{NP} method are given below:

$$A = \frac{I_1 I_2^\infty}{I_2 I_1^\infty} \quad (1) \quad B = \frac{L_{1,1}}{L_{2,1}} \quad (2) \quad C = \frac{L_{1,1}}{L_{1,2}} \quad (3)$$

$$T_{R \rightarrow \infty} = \frac{0.74 A^{3.6} \ln(A) B^{-0.9} + 4.2 A B^{-0.41}}{A^{3.6} + 8.9} \quad (4) \quad T_0 = R_{NP} [(ABC + 1)^{\frac{1}{3}} - 1] \quad (5)$$

$$\alpha = \frac{1.8}{A^{0.1} B^{0.5} C^{0.4}} \quad (6) \quad \beta = \frac{0.13 \alpha^{2.5}}{R_{NP}^{1.5}} \quad (7)$$

$$T_{R \sim 1} = \frac{T_{R \rightarrow \infty} R_{NP}}{R_{NP} + \alpha} \quad (8) \quad T_{NP} = \frac{T_{R \rightarrow \infty} + \beta T_0}{1 + \beta} \quad (9)$$

where I_i is the measured XPS intensity from a material, where $i=1$ indicates the shell material, and $i=2$ indicates the core material. The measured or estimated XPS intensity from a planar sample of pure material is denoted by I_i^∞ . The effective attenuation length of an electron from material b travelling through material a , is denoted by $L_{a,b}$ where a or $b = 1$ indicates the shell material, and a or $b = 2$ indicates the core material. The nanoparticle radius, R_{NP} , is given in units of $L_{1,1}$ – users should be aware that all dimensions for this method are considered in units of $L_{1,1}$, as is the calculated thickness, T_{NP} , returned. The effective attenuation lengths required can be estimated directly using formulas from the work of Seah³¹ or the values of B and C can be estimated using the following approximations³¹:

$$B = \left(\frac{E_1}{E_2} \right)^{0.872} \quad (10)$$

$$C = \left(\frac{Z_2}{Z_1} \right)^{0.3} \quad (11)$$

where E_i is the kinetic energy of electrons from material i , and Z_i is the (atomic-concentration-averaged) atomic number of material i , for $i = 1$ indicating the shell material, and $i = 2$ indicating the core material

– for organic materials, an estimate of $Z = 4$ is likely appropriate³¹. By combining these formulae step-by-step, the user can thus obtain an estimate for the nanoparticle shell thickness, having started simply with knowledge of the core and shell materials of the sample, the according experimentally measured XPS intensities and an estimate of the total diameter. The composition of the core and shell materials are also, in theory, accessible from the XPS data itself. For optimal results, reference intensities from samples of the pure core and shell materials should be measured in the same instrument ideally at a close point in time, to minimise variation in transmission function. Reference samples should be both as clean and as flat as is possible. The error in the calculated thickness using this method is typically on the order of ~4%, which is smaller than the expected error in the estimation of the effective attenuation lengths²⁹.

This method has also been extended to produce an iterative method for calculating shell thicknesses for core-shell-shell nanoparticles²⁸. Both core-shell and core-shell-shell calculations can be also be used with multiple elements present in the core and/or shell by estimating attenuation lengths using an average of the materials present (weighted according to stoichiometry) and then calculating the estimated shell thickness separately for each core/shell element pair ratio. This can also be used to determine an estimate for the stoichiometry, by iteratively solving element fractions for each material in order to minimise the deviation between thickness estimates. A practical example of this is given in the paper detailing the core-shell-shell method²⁸.

Using the T_{NP} method and related methods, it is assumed that the sample under study consists of an array of randomly oriented spherical nanoparticles, for which the core and shell(s) consist of uniform distributions of material. For non-uniform shells, dislocated cores, and similar such morphologies, this method will typically underestimate the shell thickness. Likewise, for populations of nanoparticles with high polydispersity in shell thickness, the estimate provided will be lower than the average shell thickness. Finally, care should be taken when applying these methods to systems where elastic scattering of electrons is expected to play a significant role (e.g. nanoparticles with thick, highly-scattering shells), as the use of the straight-line-approximation in developing these formulae mean that the effects of elastic scattering are not considered³².

An Excel spreadsheet designed to simplify the use of this method, capable of calculating overlayer thicknesses for both planar and nanoparticulate samples from XPS data, can be found on the NPL e-learning site as a part of the ‘Measuring the Surface Chemistry of Nanoparticles using XPS’ short e-learning course¹⁷.

4.3 SIMULATION OF ELECTRON SPECTRA FOR SURFACE ANALYSIS

In circumstances where more complex morphologies of nanostructure need to be analysed, or greater accuracy with respect to elastic scattering effects is required, the NIST database for the Simulation of Electron Spectra for Surface Analysis (SESSA) has been reported to be an effective method³³. The software may be used to generate simulated AES and XPS spectra and/or peak intensities for a range of nanostructures with multiple overlayer films^{34,35}. The user may specify the morphology and components, then run a simulation for a range of dimensions (e.g. such as nanoparticle overlayer thickness) in order to determine the point of maximum agreement between the simulated peak intensities and experimentally measured data.

SESSA contains databases of values for many of the physical parameters relevant to XPS analysis such as inelastic mean free paths, photoionisation cross sections, scattering cross sections, etc. Multiple sources are provided for several of these parameters, typically including both empirical and theoretically calculated datasets. References for these are provided, such that the user may verify the applicability of any given parameter set, and select those most appropriate for their simulation. Many of these values can also be changed directly by the user. The user may also choose to ‘turn off’ elastic scattering, allowing determination of the strength of elastic scattering effects on resultant spectra for a given system.

Of the three methods discussed here, SESSA professes to utilise the most comprehensive theoretical backing, and is ostensibly simpler to use than manual numerical modelling. As with the use of numerical modelling however, the versatility provided by SESSA must be used with care, as multiple distinct

configurations of composition and morphology may be found to match a given experimentally-obtained spectrum. It is always advisable that as many possible parameters of a nanoparticle system are determined experimentally by complementary analysis techniques rather than varying these within a model. This will help minimise the risk of converging upon a solution that matches experimentally observed intensities but with an incorrect model of the system.

Comparisons between SESSA and methods such as the T_{NP} formula have shown good agreement for a range of well-defined nanoparticle models. Significant disagreement was noted only for systems in which elastic scattering effects may be significant, when SESSA modelling was performed taking these effects into account²⁷. With appropriate supporting measurements to elucidate the structure of a system, modelling using SESSA has been shown to match experimentally observed XPS intensities within reasonable uncertainty³⁶.

4.4 SUPPORTING MEASUREMENT TECHNIQUES

In order to determine the average particle diameter, as required for shell thickness calculations, several techniques may be used³⁷. However it is vital to ensure that the related limitations of these techniques are known.

Dynamic Light Scattering (DLS) is one of the more common sizing techniques available for measuring nanoparticle size in solution. DLS measures the hydrodynamic diameter, and typically over-estimates the physical particle diameter by up to about 8 nm. Furthermore, DLS results are strongly skewed by effects such as agglomeration and polydispersity, so should only be trusted in cases where monodispersity is certain. High-resolution techniques such as centrifugal photosedimentation may be used as a support in order to confirm monodispersity, in which case the average size measured by the cumulant method in DLS is typically a reasonable approximation. Electron Microscopy techniques may provide a reasonable estimate of nanoparticle diameter, assuming a large enough sample of particles can be measured to obtain a reasonable estimate of the population size distribution. Care must be taken if using electron microscopy on organic or organic-coated nanoparticles, as beam damage is likely for such materials and may affect the sizes measured. Table 4 below lists several of the common supporting measurement techniques used alongside XPS, as well as their benefits and disadvantages.

Surface analysis techniques other than XPS may also prove useful in the analysis of nanoparticles and nanoparticle coatings. Using low-energy ion scattering (LEIS) and measuring the energy loss of backscattered ions from the core of a nanoparticle can be used to determine the coating thickness of particles with a heavy element in the core^{38,39} and has been shown to provide reasonable agreement with XPS measurements of the same nanoparticles²². Medium-energy ion scattering can also be used to determine shape and size distribution of nanoparticles^{12,40}. Several of the guidelines for sample preparation as laid out in this document apply, in general, to other vacuum-based surface analysis methods, but do not account for any particular issues faced by such techniques (e.g. the requirements for MEIS that the sample is in the form of a sub-monolayer).

Technique	Benefits	Disadvantages
Electron Microscopy	Can provide information on size and shape of particles to support/refute assumed morphology and improve simulation/modelling. For some samples TEM may provide core size/shape.	Statistically representative measurements can be time-consuming or impractical to obtain. Many particles or coatings, particularly organics, may be damaged by electron beam
Atomic Force Microscopy	Can provide topography, size measurement	As with EM, statistically significant measurements can be time-consuming
Dynamic Light Scattering	Can provide size of particles	As a solution-based technique, measurements are not necessarily equivalent to samples under vacuum.
Differential Centrifugal Sedimentation	Can provide high-resolution size distribution of particles, i.e. information on polydispersity	As a solution-based technique, measurements are not necessarily equivalent to samples under vacuum. Can prove difficult for samples with density close to that of water.
Nanoparticle Tracking Analysis	Can provide size of particles	As a solution-based technique, measurements are not necessarily equivalent to samples under vacuum.
Ion Scattering	Can be used to provide measurements of overlayer thickness, and can identify the presences of uncoated core, i.e. pinholes, incomplete shell coverage ^{22,38,39}	Typically requires a high-Z core, low-Z shell.
Small Angle X-ray Scattering	Can identify size and structure of a population of nanoparticles	Requires complex modelling, and like for non-ideal systems
Single-Particle Inductively-Coupled-Plasma Mass-Spectrometry	Can provide size distribution and elemental information	Elemental information limited, minimum particle size detectable controlled by analyte sensitivity
Scanning Transmission X-Ray Microscopy	Can provide information on size and shape of individual particles, image contrast based on chemical composition, less beam-induced damage than electron beam based methods	Statistically representative measurements are time-consuming, Spatial resolution lower than electron microscopy

Table 4 - Summary of techniques complementary to XPS surface analysis

5 CASE STUDY – VAMAS TWA 2 PROJECT A19 INTERLABORATORY STUDY FOR XPS

A VAMAS interlaboratory study was carried out in 2015 on the measurement of thickness and chemistry of nanoparticle coatings. The primary aim of this study was to determine the reproducibility, between laboratories and instrument models, of XPS measurements of nanoparticle coatings. This was achieved with the collaboration of 25 surface analysis laboratories around the world. Each laboratory was sent

two types of nanoparticle sample: one of an aqueous suspension of gold nanoparticles coated with a peptide; the other was a deposit of the same particles on a silicon wafer, prepared at NPL using the protocols described at the end of this document. Participants were provided with a cleaned silicon wafer and o-ring for use in the deposition of their own sample from suspension - a full copy of the information provided to participants was published as NPL Report AS 95, "VAMAS TWA 2: Project A19: Inter-laboratory study of the measurement of chemistry and thickness of nanoparticle coatings: Protocol for sample preparation"⁴¹.

In brief, it was found that good reproducibility occurred if the samples prepared at NPL were measured by each laboratory and those measurements were interpreted at NPL. Local approaches led to variability but the XPS analytical method was sound.

Sample preparation was found to be a major source of variation between laboratories. Many laboratories lacked a vacuum desiccator leading to extremely long total deposition times, while some participants also lacked pipettes of the required precision, resulting in large, uneven deposits. Overall, this led to a broad variety of observed sample deposits, a range of which are shown in Figure 7.

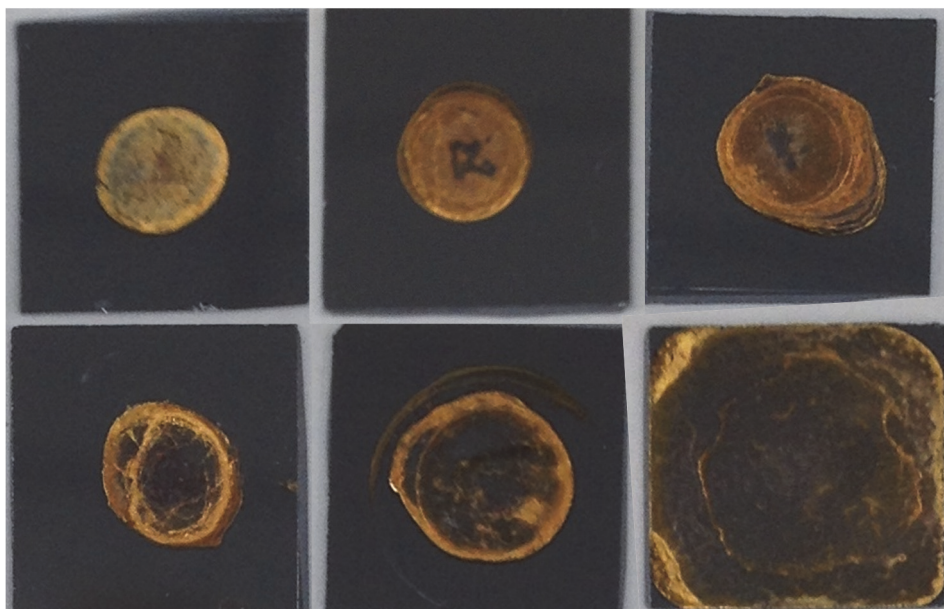


Figure 7 - A range of example deposits of the same nanoparticle system. Samples were all deposited onto approximately 1 cm square pieces of silicon wafer from matching suspensions by different laboratories and were imaged, later, at NPL. The top left shows a relatively even and thick deposit, similar to that of the pre-prepared samples provided to participants (as shown in Figure 4), while the bottom left sample shows an uneven, patchy deposit.

Thicknesses measured using consistent analysis technique between both pre-prepared and participant-prepared samples showed significant discrepancy, with those samples prepared by participants having a consistently larger estimated thickness. A significant decrease in the signal from the nitrogen in the shell material was also observed with these samples, indicating that the increased thickness estimates were likely due to a combination of contamination and degradation occurring at some point in process of transport, storage, and deposition of the nanoparticle suspensions. This highlighted the importance of both consistent deposition protocols and, at least for organic-containing particles, that preparation for analysis happen as soon as possible after creation.

The significant contributors to variability in the analysis were found to be from transmission function correction, choice of sensitivity factors, and choice of analysis method. For the pre-prepared samples distributed by NPL, the scatter between thickness estimates from participants was large, with a relative standard deviation of ~67%. When raw data was analysed using consistent methodology and sensitivity factors, the variation between calculated thicknesses for the same samples was approximately 10%.

indicating the significant impact that reference data and calculation method have on the estimated thickness. Figure 8 shows the variation between thickness estimates made using survey data from a number of participants. This data is from the pre-prepared samples distributed to the participants, and the analysis was performed at NPL with the T_{NP} method using Au 4d peaks for the core, for which variation in instrumental transmission between the participants was observed to be minimal.

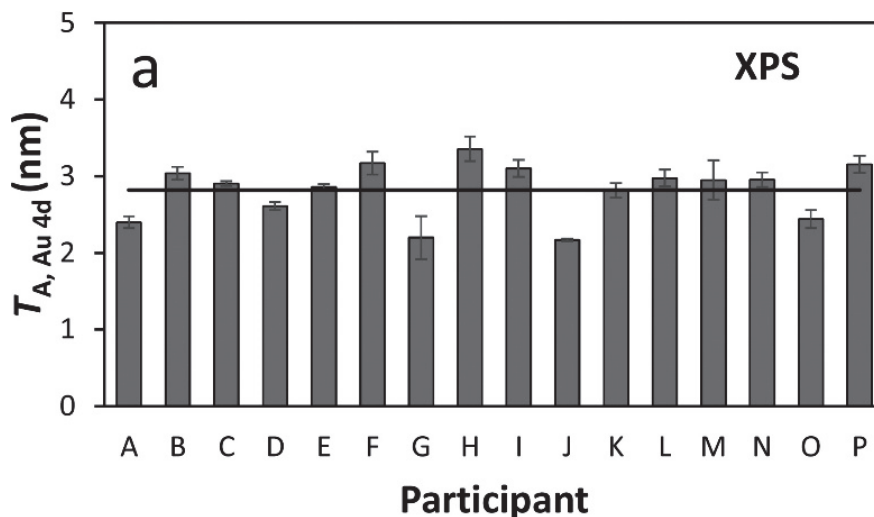


Figure 8 - Comparison of thicknesses for pre-prepared samples calculated using Au 4d peak from participants' survey data. The solid line indicates the average value.

Of the issues highlighted by this study, the variation introduced by differences in transmission function correction and sensitivity factors is an issue for XPS analysis of any samples. When analysed at NPL, the sensitivity factors used were the Average Matrix Relative Sensitivity Factors (AMRSF) which are available for public use from the NPL website⁴². It was noted that use of SESSA by participant P to calculate reference intensities resulted in a measurement that was insignificantly different to that calculated using flat reference materials on an instrument with a calibrated transmission function using the NPL AMRSF's.

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7 APPENDIX: PROTOCOLS

7.1 SILICON WAFER SUBSTRATE PREPARATION PROTOCOL

Presented below is a step-by-step substrate cleaning protocol that is commonly used by the NPL Surface Technologies group prior to nanoparticle sample deposition. This protocol is predominantly used for silicon wafer, but may be applied or adapted for other substrate materials.

- 1) Cut wafers to desired size and shape, typically ~10x10 mm, using a diamond scribe
- 2) Remove larger adhered dust and contaminants by wiping with laboratory tissue (or similar) soaked in a small quantity of iso-propyl alcohol.
- 3) (Optional but recommended) Observe substrate surface using an optical microscope, if significant dust or other particulates remain, carefully repeat step 2.
- 4) Ultra-sonicate substrates in isopropyl alcohol for 15-20 minutes to remove more strongly adhered contaminants

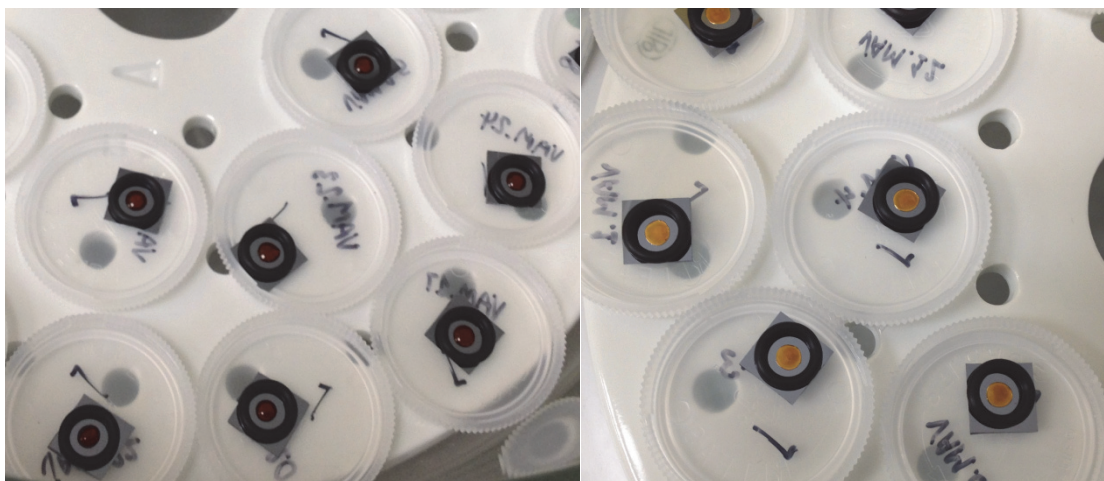
- 5) Remove substrates from the isopropyl alcohol, and dried under a stream of nitrogen or argon.
- 6) Substrates are then cleaned using UV-ozone treatment for 15-20 minutes (Note: This step produces an extremely hydrophilic surface on the silicon wafer, which may or may not be desirable. Some substrates may not be suitable for UV-ozone treatment)
- 7) Substrates are now ready for sample deposition.

When even greater cleanliness is required, the ultra-sonication in iso-propyl alcohol may be replaced with cleaning using aggressive oxidising solutions such as Piranha or similar. Alternatively, the 'RCA Clean'⁴³, used extensively in the semiconductor industry for wafer cleaning prior to high-temperature processing, may be used to achieve a clean and well-defined substrate surface.

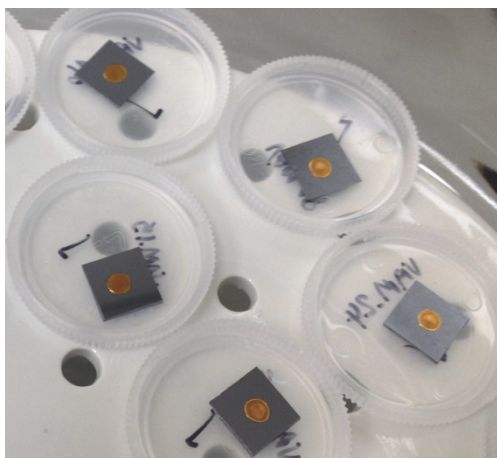
7.2 DROP-CASTING PROTOCOL USED IN VAMAS TWA 2 PROJECT A19 INTERLABORATORY STUDY

The following text and images are taken from the deposition protocol recommended for participants of a VAMAS interlaboratory study on the measurement of the chemistry and thickness of nanoparticle coatings:

The aqueous solution of nanoparticles should be applied to the silicon wafer supplied using the Viton rubber O-ring to reduce 'coffee ring' drying effects. We recommend placing the O-ring at the centre of the silicon wafer and applying a 3 μL aliquot of sample solution centrally, within the confines of the O-ring (without touching the sides). The O-ring serves to reduce differential evaporation rates, so do not simply fill the O-ring with liquid; the sample solution must not contact the O-ring. Allow the solution to dry before applying subsequent aliquots over the top of the dried residue. Continue this process until all of the solution has been utilised. This process may be performed in a desiccator to speed up the drying process, however please ensure the environment is clean and application/removal of vacuum is applied with extreme caution to avoid disturbing the deposited dried material.



Above: Photographs of nanoparticle solution during the deposition process - droplets should be placed within the O-ring as shown in the left picture. After multiple cycles of deposition and drying, a circular area of deposited nanoparticles as shown in the right picture should begin to be seen. Upon completing the deposition, carefully remove the O-ring, and the sample should appear as in the picture below.



If analysis will not be performed immediately, the sample may be stored in an argon-filled plastic bag sealed and placed in a fridge.

7.3 SPIN-COATING PROTOCOL USED FOR POLYMER CORE-SHELL NANOPARTICLES

The following protocol for silicon wafer cleaning and subsequent spin-coating of polymer core-shell nanoparticles was used at BAM to produce high-quality nanoparticle deposits for XPS. Figure 5 shows SEM micrographs of an example deposition of such nanoparticles.

- 1) Wafer purification:
 - i) 10 min sonication in 2% aqueous *Hellmanex*® *III* solution
 - ii) Dry under nitrogen
 - iii) 10 min sonication in iso-propyl alcohol
 - iv) Dry under nitrogen
 - v) 10 min sonication in iso-propyl alcohol
 - vi) Dry under nitrogen
 - vii) 10 min sonication in ethanol
 - viii) Dry under nitrogen
 - ix) 20 min UV/Ozone treatment
- 2) Spin coating of one 30 μ L droplet of nanoparticle suspension
 - i) Place cleaned wafer in spin coater
 - ii) Place one 30 μ L drop on centre of stationary wafer
 - iii) Run the following program:
 - iv) Spin to 1000 rpm at 333 rpm/s, maintain 1000 rpm for 2 s (total 5 s)
 - v) Spin to 2000 rpm at 1500 rpm/s, maintain 2000 rpm for 19.4 s (total 20 s)
 - vi) Decelerate to 0 rpm at 666 rpm/s, (total 3 s)
 - vii) Remove sample from spin-coater

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