RESEARCH ARTICLE | MARCH 06 2020

Guide to making XPS measurements on nanoparticles

Special Collection: Special Topic Collection: Reproducibility Challenges and Solutions

Donald R. Baer

Journal of Vacuum Science & Technology A 38, 031201 (2020)
https://doi.org/10.1116/1.5141419

JVST A
Journal of Vacuum Science & Technology A

TUTORIAL

avs.scitation.org/journal/jva

Guide to making XPS measurements on nanoparticles

Cite as: J. Vac. Sci. Technol. A 38, 031201 (2020); doi: 10.1116/1.5141419
Submitted: 5 December 2019 · Accepted: 11 February 2020 ·
Published Online: 6 March 2020

Donald R. Baer

AFFILIATIONS

Pacific Northwest National Laboratory, P. O. Box 999, Richland, Washington 99354

Note: This paper is part of the Special Topic Collection on Reproducibility Challenges and Solutions.

ABSTRACT

This guide briefly summarizes issues and considerations important for the use of x-ray photoelectron spectroscopy (XPS) for characterizing nanoparticles, which are important in many areas of science and technology. Because the surfaces play a major role in determining nanoparticle behaviors, XPS is an increasingly useful tool for understanding their properties, including addressing variations and nonreproducibility issues associated with these materials. The unusual physical and chemical behaviors of these particles must be considered in preparing and characterizing these materials. This guide is one of a series intended to highlight the best practices in the use of XPS.

I. INTRODUCTION

Nano-objects, with size between 1 and 100 nm in at least one dimension,[1] are important in many areas of scientific research and technology, development, and application.[2,3] In a review of characterization of these materials, Linkov *et al.*[4] comment that "The study of nanostructures and nanomaterials requires special protocols that take into account the physical phenomena that only occur in nanosized systems." This guide focuses on the issues that need to be considered when applying x-ray photoelectron spectroscopy (XPS) to obtain important surface and other information about these materials and is one of a series of XPS guides intended to assist users by providing information about good practices in the use of XPS.[5]

Although this guide focuses primarily on nanoparticles (NPs), much of the material applies broadly to other types of nano-objects and other types of nanomaterials.[1] In addition, the importance of XPS analysis of particles extends to sizes larger than 100 nm and many of the topics discussed in this guide will apply to larger particles. The US Food and Drug Administration considers that particles may dimensionally determine properties (a nanoparticle type behavior) for sizes up to at least up to 1000 nm.[6]

As NPs have a very high surface-to-volume ratio, their surface properties strongly influence and in many cases control their behaviors.[7,8] As the field develops, NPs are designed with increasingly complex structures, involving multiple layers and designed functionalization for a variety of applications. However, researchers doing surface science know that surface chemistry and composition can be very difficult to control and NPs have a further complication of often changing in response to their history, processing and storage, age, and environmental conditions (chameleon effect).[9,10] As a result of these and other issues, characterization of NPs and other nano-objects is increasingly recognized as having a variety of challenges.[11–15]

XPS is an important tool for understanding the nature of NP surfaces as well as the structure and thickness of coatings on NPs. It can be used in different ways to extract important information including the composition of the NPs, presence of contamination, the consistency of functionalization, the quantity of adsorbates on surfaces, and the thicknesses of layers and coatings.[2,16–19] The level and approach to XPS data collection and analysis depend on the specific question being asked of the measurement. As noted by Shard,[20] two of "the major problems in XPS analysis of nanoparticles are the preparation of samples for analysis and the interpretation of data."

The objective of this introductory guide is to identify issues or topics to be considered for XPS analysis of nanoparticles. It is not intended to provide all the relevant details but point to literature or other references that can provide needed information. Topics briefly discussed include (a) XPS measurement objectives, (b) awareness of potential sample alterations including effects of handling and probe damage (c) timing—when to make the measurement and information to retain and report, (d) sample preparation, and (e) analysis approaches.

II. MEASUREMENT OBJECTIVES/DESIRED INFORMATION

The approach needed for XPS analysis of nano-objects depends on the needed or desired information. Possible analysis objectives, with increasing levels of analysis complexity, include:

(i) Qualitative information—*What are the particles made of and what is on their surface? Is there unexpected contamination? Do elements on the surface have the expected chemical state?* These questions are qualitative and sometimes depend only on the presence or absence of detectable visible signals. As one example, breakdown products of polytetrafluoroethylene (PTFE) were identified on the surface of Cu-oxide nanoparticles as a consequence of the nature of the synthesis process.[2] It is useful to remember that the XPS information depth is dependent on the energy of the photoelectron and material, but nominally considered to be about 10 nm. For particles of this size and being smaller, XPS is sensitive to the surface and bulk composition of the particles and will generally sense the particle surface, the presence of coatings, and usually some portion of the particle core.

(ii) Comparative quantitative information–*How much contamination is present? Are the particles made or examined today the same as those examined yesterday, last week, last month? Is the surface functionalization of particles consistent from batch to batch?* In many cases, these questions can often be answered by "standard" approaches to XPS quantification. The inability to establish consistent functionalization of particle surface is an example of this type of use and analysis.[17,21]

(iii) Quantitative chemical and physical structural information—*What is the thickness of the surface layer on the particles? Does the particle have a multiple layered structure? What is the thickness of a contamination layer?* Greater detail about the nature of nanoparticles can be extracted by using a variety of data analysis and modeling approaches. Quantification of the thickness of single or multiple surface coatings using detailed modeling approaches is an example of this type of application.[18,22]

The questions to be answered and the source or nature of the particles influence the approaches needed for sample preparation and the type and extent of data to be collected. Dry particles for which the analysis objective is to determine what is present on the sample may not require sample cleaning and much of the analysis might be extracted from survey spectra. In contrast, particles suspended in a complex solution for which the structure and thickness of surface coatings are the analysis objective would require removing the sample from solution, efforts to remove extraneous surface residue from the solution preserving the particle surface composition and chemistry as far as possible, and efforts to make sure that all important elements expected in the coatings are included in a detailed analysis.

III. SAMPLE CHANGES AND ALTERATIONS

It is very common for nanoparticles to have differences in composition, size, and surface chemistry from what was intended or expected.[10,23] Among the reasons for this are small or uncontrolled changes in the synthesis process,[24] the importance and challenge of obtaining consistent surface chemistry,[7,9,21] and the ease of nano-objects to change in response to environmental conditions, handling or when subjected to experimental probes.[14,25,26] Although not all particles or objects change due to aging, handling, storage, or measurement conditions, it is useful to establish or verify the relative stability of any set of nano-objects being examined in relation to the history, handling, and desired use of the particles.

IV. TIMING AND PROVENANCE INFORMATION–WHEN TO MAKE A MEASUREMENT AND INFORMATION TO RECORD

Because characteristics of nanoparticles are often influenced by details of the synthesis route, sample storage, sample handling and processing, and the nature of any dispersion media,[10] the timing of measurements is relevant to the questions to be addressed by XPS. Typical questions and timings include (a) immediately after synthesis to verify the nature or consistency of the synthesis process; (b) after sample processing to verify impacts of the processing including: contamination/cleanliness, consistency or nature of surface functionalization; c) before any use or application to verify particle status.

Due to the potential impact of sample synthesis/storage/processing/handling history on the nature of nanoparticles and their surfaces, it is important to retain information about particle history, the timing of characterizations, and characterization details and results. This history is sometimes called *provenance information* and is an important component of authenticating the nature of a collection of nanoparticles or other nano-objects.[27,28] As part of the information record and to help with reproducibility questions, it is also important to record details of XPS measurements including the instrumentation used as well as data collection and analysis parameters (pass energy, sensitivity factors, transmission function information).

V. SAMPLE PREPARATION

The overall objective of sample preparation, as suggested in Fig. 1, is to get the initial sample, however received, into the form

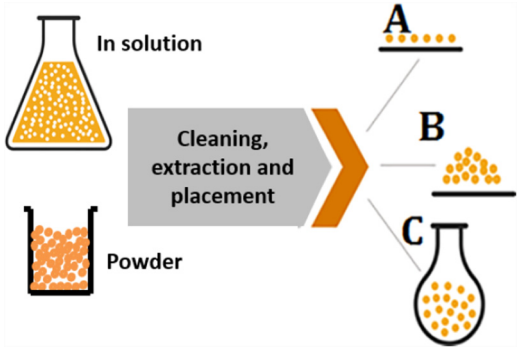

FIG. 1. The objective of sample preparation is to get the as received samples into the form needed for analysis while minimizing sample changes that would hide the desired information. Adapted with permission from D. R. Baer and V. Shutthanandan, *Comprehensive Biomaterials II*. Copyright 2017 by Elsevier.[1]

needed for analysis without destroying or changing the information that is desired from the measurement. In some circumstances, it is necessary to handle samples in controlled environments to stop or minimize sample changes that may occur due to environmental exposure.

An important issue in preparing solution-dispersed particles for analysis arises because most particles in solution are surrounded by a complex mixture of solution species, including ions and organic molecules. The challenge is to remove particles from the surrounding solution while minimizing contamination from the solution and retaining any coating attached to the particles. A variety of processes have been successfully used with differing degrees of effectiveness. Many of these have been summarized as part of ISO standard 20519-4.[27,29] A book chapter on the preparation of nanoparticles for surface analysis includes summaries of several examples protocols for preparing NPs by other relevant sample preparation processes.[30]

As shown in Fig. 1, particles may be received in solution or as a powder. Depending on the analysis need, they may need to be cleaned/washed, suspended in solution, or deposited on a substrate. Fortunately, for many types of XPS analysis, a random pile of particles, as shown in Fig. 1(b), is satisfactory for detailed XPS characterization using what is called the single-sphere-model.[31] For analysis objective (i), (ii), and some approaches to (iii), it is usually important for the collection of particles to fully cover the substrate so that only signals from the NPs are detected. Limitations to the single-sphere-model and an example of a need for sample preparation type [Fig. 1(a)] are discussed in Sec. VI. Often it is desirable to run multiple types of analysis on a batch of NPs and identical or similar processing may be needed for multiple types of sample geometries as suggested in Fig. 1.

A. Washing and separation from solution

Washing and separation of NPs from solutions are frequently accomplished by (i) *dialysis*, (ii) *centrifugation*, (iii) *diafiltration* or a combination of them as schematically shown in Fig. 2. A "*flash dry*" filtering and washing process has been successfully used for particles to be extracted from a reactive environment. The specific process to be used depends on the experience and capabilities of the relevant laboratories and the nature of the samples. Centrifugation, for example, of low density or 5–10 nm particles can be time consuming and inefficient. The longer times required for dialysis may be incompatible with unstable particles or unstable coatings on particles.

Dialysis and *diafiltration* are sometimes used in parts of nanoparticle synthesis protocols. Techane *et al.* used dialysis for removing excess thiol and ions from AuNPs in solutions that had been coated with a self-assembled monolayer (SAM),[32,33] finding that the particles were more effectively purified by dialysis than the more common centrifugation method, described below.

The *centrifugation* method involves concentrating particles in part of the solution, poring off the supernatant that does not contain the particles, and resuspending the particles in clean solution. This may be done multiple times to accomplish the desired cleaning by removal of soluble impurities.[34] *Diafiltration* is a continuous flow filtration system that Sweeney *et al.*[35] found to be faster and to produce nanoparticles of higher purity than often possible by dialysis or a combination of solvent washes and centrifugation.

It is natural and appropriate to ask how much cleaning is needed and which process is the most effective. La Spina *et al.*[36] directly addressed both of these questions for citrate stabilized AuNPs. They found both centrifugation and dialysis to be effective in cleaning particles, with two centrifugation cycles equivalent to 12 four-hour dialysis cycles. In their studies, the particles prepared with centrifugation were more effectively functionalized with 1H,1H,2H,2H-perfluorodecanethiol hydrophobic thiols than either unwashed or those processed by three dialysis cycles. It is also relevant to know that several researchers have found that after three centrifugation/wash cycles, particles aggregate more easily and may not be readily dispersed.[36,37] We have found it informative to examine particles at various stages of whatever cleaning process is used to understand the extent of cleaning that is useful or effective.

The *flash drying filtering* process described by Nurmi *et al.*[38] was designed to examine particles that are reactive in solution and to stop such processes for analysis. In the flash-drying method, particles were removed from the solution in a controlled atmosphere glove box using a standard vacuum filtration apparatus. After the

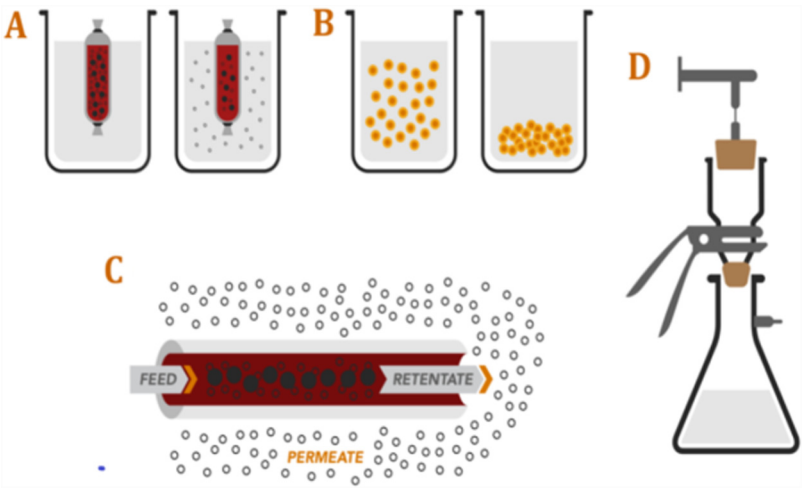

FIG. 2. Methods used to separate and clean nanoparticles supplied in a solution include (a) dialysis, (b) concentration by centrifugation, (c) diafiltration, and (d) filtering/flash drying. Reprinted with permission from D. R. Baer and V. Shutthanandan, *Comprehensive Biomaterials II*. Copyright 2017 by Elsevier.[1]

particles were poured into the filter to remove the original solvent, they were rinsed with a hygroscopic solvent such as acetone. We have also found that filtering can be used to isolate particles that are changing chemical state as a function of time.[26]

Some carbon residue usually remains on NP surfaces after the cleaning processes. With care, the amount of this contamination can be minimized, and it is useful to monitor and compare the extent of contamination to see if processes remain effective or can be improved. In the studies by Wang *et al.*[37] on Ag NPs, the contamination layers had an effective thickness of 0.05 nm or less.

B. Deposition approaches

Many types of surface and other analysis methods require NPs to be supported on a substrate. Issues associated with particle deposition include the nature of the substrate in the context of the analysis questions, the analysis requirements, and the deposition process to be used.

1. Substrates

The specific substrate to be used depends on the nature of the sample and the analysis questions. A variety of substrates have been used for XPS analysis. Often the substrate is selected based on the experience and expertise of the analyst involved. Clean versions of gold, carbon, silicon, indium, polycarbonate filters, and PTFE are among substrates in common use. Issues of importance are the cleanliness of the substrate and potential for XPS peaks from the substrate to interfere with those from the sample.

Silicon wafers are often used because they are durable, easily cleaned, and usually quite flat. If there are sufficient particles to totally cover the substrate, cleanliness may not be critical, but there are established methods for thorough cleaning of silicon wafers.[39] One potential issue for a cleaned silicon wafer is the creation of a hydrophilic surface that may complicate getting good surface coverage, leading to the formation of what are often called coffee rings when depositing solutions on the surface by drop coating.

PTFE can be a good substrate choice because it exhibits low hydrocarbon contamination with a carbon peak from CF_2 significantly far from the C 1s peaks present in many NPs.[19] The nonconducting nature of PTFE is one disadvantage.

2. Solution deposition

Common methods for depositing NPs from solution on the selected substrate include drop coating, spin coating and sample dipping, with drop coating of particle suspension being the most common.[34,40]

Drop coating is achieved by placing small drops of liquid containing the NPs on the substrate and letting the solution dry. Multiple deposits can be used to produce a layer that fully covers the substrate for XPS analysis without signal interference from the substrate. Sometimes small clean O-rings are used to surround and contain the drop-casting deposits.[41] Belsey *et al.*[41] conducted an interlaboratory comparison study involving measurement of peptide coatings on Au NPs and found that the sample deposition and preparation processes were a challenge to many research teams. This highlights the need for care and consistency during this process and the need to verify that the processes used are producing useful deposits. In their work,[42] a vacuum desiccator was used to speed the drying process. Vacuum assisted drying also helps minimize carbonaceous contamination by speeding the drying process and minimizing the amount of impurities taken up by the liquid that end up on the particle surfaces.

Spin coating has been used successfully to produce useful coatings when there is difficulty with the drop-casting process.[42,43] One advantage of spin coating is the ability to control film thickness, but the process requires a significant amount of the sample, and experimentation is required to establish the spin-speed curves to achieve the desired deposits.

Solution dipping and drying can be used to deposit low densities of particles on a substrate and thus less useful for many XPS measurements with low lateral resolution. However, it can be used for measurements of individual NPs, such as possible by photoemission electron microscopy, some high resolution synchrotron based photoemission measurements, and those performed by transmission electron microscopy (TEM), scanning electron microscopy studies, and in some circumstances time-of-flight secondary ion mass spectrometry.[44]

3. Dry particle deposition

The methods most often used for deposition of dry NPs are those historically used for powder analysis.[45–47] The approaches often involve (a) the use of double-sticky tape, (b) placing particle in some type of holder or containment device, or (c) compressing the particles onto a substrate (adhesive tape or soft foil such as indium) or forming a free-standing pellet.

The use of *double-sticky (adhesive) tape* is very common. The Lochner[46] description of powder mounting describes the process of using double-stick carbon tape as often used for XPS analysis. Conducting carbon and copper tapes are often used with the advantage of being conductive. However, standard double sticky (such as 3M 665 for mounting photographs) is often used at Pacific Northwest National Laboratory by covering the tape fully with the NPs or other powders. Although this tape is nonconducting, excellent data have been collected involving the use of the neutralization system in a Phi Quantera instrument.

A specialized *container/holder* has been developed for mounting powders for XPS by Hellgardt and Chadwick.[45] Their holder constrains the particle to a small cup with a cover (containing a pump-out hole) to minimize particle loss during sample movement.

Appropriate care and following the local safety regulations are particularly relevant in the handling of dry NPs to avoid health risks that may be associated with particle inhalation.

VI. ANALYSIS NEEDS AND APPROACHES

As would be expected, the measurement objectives determine the type of data that needs to be collected and the analysis needed. If the desired information is primarily the identification of contaminants on NP surfaces (and the sample has been appropriately prepared), the elements or chemical states present in the survey or high-energy resolution XPS spectra can be determined using standard methods of peak and chemical state identification. Similarly, the determination of consistency in synthesizing or functionalizing

a set of NPs of the same size might be validated by a consistent determination of the relative intensities of photoelectron peaks or application of standard XPS quantification procedures without detailed consideration of the geometry of the particles.

However, since the nanostructure of the sample influences photoelectron peak intensities and relative peak intensities, peak energies, and background signals,[16] it is possible to invert the process and use XPS spectra to learn a good deal about the nature of NPs. With some work, proper data collection, and modeling, it is possible to learn information about particles sizes,[48,49] single and multiple coating and shell thicknesses,[18,50–52] and the extent or nature of surface functionalization.[40,53]

The major difference between analyzing flat and NP surfaces is shown schematically in Fig. 3. Because electrons from the "core" of an NP need to travel a variety of different distances to reach the analyzer, the ratio of coating to substrate photoelectron signals will vary with particle size. For particles smaller than ≈10 nm, XPS senses both the top and some of the bottom of a particle. As the particle size increases, the "visible" top of the particle will be sensed by XPS and the relative signal strengths,[16,54] and the nature of the inelastic background[55] will increasingly look the normal emission analysis condition shown as the first component of Fig. 3.

One of the important needs for quantitative XPS analysis of nanoparticles is the determination of the thickness of layers on nanoparticles. The thicknesses of layers can be determined using modeling approaches (see Ref. 56 for a summary of some relevant XPS modeling programs and Ref. 57 for examples) with some assumptions and knowledge of particle size.

In both Figs. 3 and 4, XPS signals from NPs are depicted as arising from a single particle. In studies by Werner, Powell, and coworkers, it has been shown that the single-sphere-model for peak intensities applies for NPs samples with random distribution.[31,58] Two limitations of this sample preparation [Fig. 1(b)] and the single-sphere-model should be noted. First, the single-sphere-model applies until the electron inelastic mean free pathlength exceeds the particle size.[31] For smaller NP sizes, more detailed analysis is needed.[58] Second, the single-sphere-model, which enables the sample prepared as shown in Fig. 1(b) to work, only applies to peak intensities and not the inelastic signals around the photoelectron peaks. It has been demonstrated that the inelastic background around photoelectron peaks generated only by the nanoparticles can be used to quantitatively determine the thickness of NP coatings.[55] In this circumstance, XPS measurements must be from disperse NPs as indicated in Fig. 1(a).

The most common approach for determining thicknesses of NP coatings or layers uses the relative intensity of peaks from the different layers and the core, as represented by the ratio *A* of photoelectron intensities from the shell and core of a core-shell NP, as shown in Fig. 4.

Shard and co-workers[20,22,59] developed a simple method for extracting shell thicknesses from core-shell nanoparticles of known core radius. The method assumes that the NPs are spherical and of identical size, i.e., with the same core radii and the same layer thicknesses. Shard *et al.* found that the effects of elastic scattering of the photoelectrons could be represented by effective attenuation lengths used to determine thicknesses of overlayer films on planar substrates. This relatively simple method was initially used to determine the shell thickness for core-shell particles[20,59] but was extended recently to core-shell-shell particles.[22]

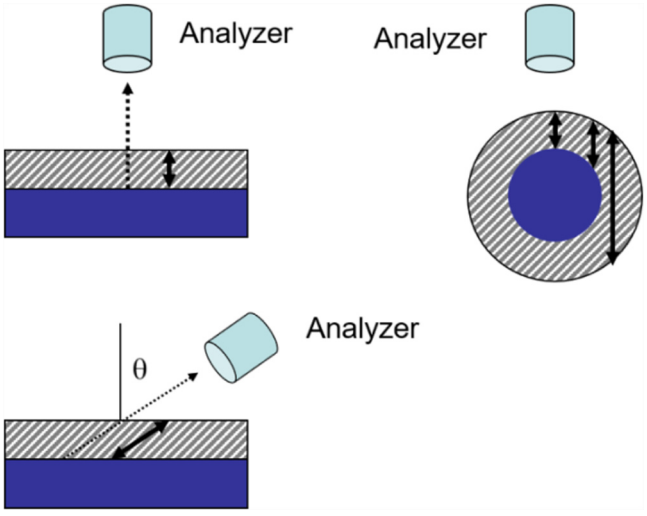

FIG. 3. Schematic drawing showing a thin coating on a flat surface and an NP. Note that there are different distances that electrons from the substrate need to travel to be detected by an analyzer. Because of the impact of the direction of electron emission from the coating on the film or particle, the ratio of signals from the coating and substrate from the film or particle will generally differ. These effects can be modeled and used to learn about the particles. Reprinted with permission from D. R. Baer and M. H. Engelhard, J. Electron Spectrosc. **178–179**, 415 (2010). Copyright 2010, Elsevier.[16]

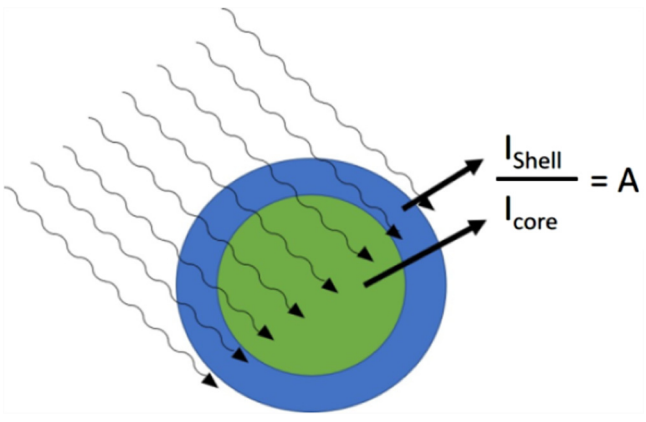

FIG. 4. Normalized intensity ratio A of photoelectron signals from the nanoparticle core and shell is the experimental data that is combined with sensitivity factors and data for effective attenuations lengths in the simple model developed by Shard to obtain the shell thickness. Adapted with permission from A. G. Shard, J. Phys. Chem. C. **116**, 16806 (2012). Copyright 2012, American Chemical Society.[20]

The Shard model uses an analytical formula that combines normalized signal intensities from the core and relevant layers with information about the relevant effective attenuation lengths to provide the layer thicknesses. Accuracy and limitations inherent in this model related to shell and coating combinations have been explored in some detail.[18,58,60] The model was found to work well for determining shell thicknesses of organic materials but to overestimate shell thicknesses for core-shell particles with strongly scattering shells.[58] Follow-up studies based on simulations of photoelectron peak intensities for Au-core/C-shell, C-core/Au-shell, Cu-core/Al-shell, and Al-core/Cu-shell NPs with a wide range of core diameters and shell thicknesses showed that values of shell thickness from the Shard equation typically agreed with actual shell thicknesses to better than 10%.[18]

The computer program and database Simulation of Electron Spectron for Surface analysis (SESSA)[61,62] contains needed data to simulate XPS spectra. Initially, the database could be used to model layered structures, but a newer version added capability for modeling nanoparticles.[31,58] Some research has been focused on understanding how best to apply SESSA to nanoparticles while others have applied SESSA to specific nanoparticle systems.

Werner *et al.*[31] used SESSA to examine the impact of different nanoparticle configurations on XPS photopeak intensities and showed that a single-particle approximation is valid for collections of NPs when the measurements with the spatial coordinates are uncorrelated. This result confirmed earlier indications[52] that a *single-particle model of relative intensities appropriately applies to measurements of a random collection (pile) of nanoparticles*. Although the single-sphere approximation breaks down when the electron inelastic mean free paths exceed the particle radius, Werner *et al.*[31] demonstrated that complex particle configurations of many types and particle sizes can be satisfactorily modeled with SESSA.

Many authors have developed models of photoelectron transport in core-shell nanoparticles in which the effects of elastic scattering were neglected. Using SESSA, Powell and co-workers[18,60] explored core-shell NPs with different material combinations to determine whether or not the neglect of elastic scattering was important. Their work showed that for organic coatings, the neglect of elastic scattering was justified.

As an example of the use of SESSA, the thickness of a 16-mercaptohexadecanoic acid ($C_{16}H_{32}$ COOH) SAM on Au NPs was examined by Techane *et al.*[32] This modeling effort showed that the SAM on Au NPs was very similar, but not identical, to the SAM on planar Au. In addition, using SESSA to model the experimental data required the presence of an adventitious carbon contamination layer, information not readily from the simple form of the Shard approach. Layer thickness determinations (with assumptions noted in the paper) were made for SAM films on Au and on Au NPs. The layer thicknesses on 14 nm Au NPs determined by SESSA were: contamination = 0.15 nm, termination functional group COOH = 0.26 nm, and 16 chain carbon units $CH_2 = 16 \times 0.09 = 1.44$ nm.

The Shard approach and the many applications of SESSA involve the assumption that the NPs are uniform in size and ideally spherical in shape. Wang *et al.*,[37] Sahoo *et al.*,[63] and Müller *et al.*[55] have explored the impacts of irregular or imperfect NPs [Ag/Au-shell/core, Au-TiO_2 particle/catalyst and PTFE-poly(methyl methacrylate) (PMMA), respectively] on XPS signals. They have found that with additional shape information from other sources such as TEM, SESSA can appropriately model the XPS data. The experimental data modeled by Yang with SESSA are available in the digital form from and published in *Surface Science Spectra*.[64] The PTFE-PMMA particles were modeled based on peak intensities using SESSA with data from sample configuration Fig. 1(b) and the Quantitative Analysis of Surfaces by Electron Spectroscopy (QUASES) program developed by Tougaard[65] using data from sample configuration Fig. 1(a). They found that the inelastic background modeled using QUASES was useful to "independently differentiate" the nonideal nature of their NP structure.[55]

VII. SUMMARY

XPS is a highly useful tool for understanding the nature and consistency of NP surfaces, and with appropriate sample cleaning, mounting, data collection, and analysis can provide important quantitative information about coatings, shells, and contamination of NPs. The full potential of XPS analysis of NPs appears to be underused.

Unfortunately, the needs for careful sample preparation and good practices for data collection and interpretation, including obtaining information from peak fitting and appropriately reporting of provenance information needed to verify particle characteristics, are too frequently ignored. Consequently, some of the XPS data from NPs reported in the literature are misleading or incorrect.

The practices highlighted in this short guide, along with good practices covered in other guides for instrument calibration, dealing with sample charging, and the recording and reporting of information can contribute important quality data and understanding of NPs properties and behaviors.

ACKNOWLEDGMENTS

This guide relies on important contributions to the application of surface methods to NPs from many people. The many and ongoing interactions with David Castner, Giacomo Ceccone, Mark Engelhard, Ajay Karakoti, Satyanarayana Kuchibhatla, Cedric Powell, Sudipta Seal, Alex Shard, and Wolfgang Unger are very much appreciated. The comments from Cedric Powell, Sven Tougaard, and Gary McGuire on the draft manuscript are much appreciated. Parts of the guide were developed based on projects in the Environmental Molecular Science Laboratory, a Department of Energy (DOE) Office of Science User Facility sponsored by the Office of Biological and Environmental Research. The planned series of guides and tutorials is being developed as part of an AVS response to reproducibility issues appearing in many areas of science. It is one of several activities being initiated under the guidance of the Reproducibility Subcommittee of the AVS Recommended Practices Committee. It is appropriate to acknowledge the large team working to develop these guides and the major contributions of members and task leaders of ASTM Committee E-42 on Surface Analysis and ISO Technical Committee 201 on Surface Chemical Analysis.

REFERENCES

[1]D. R. Baer and V. Shutthanandan, "Nano-objects as biomaterials immense opportunities, significant challenges and the important use of surface analytical methods," in *Comprehensive Biomaterials II*, edited by P. Ducheyne, D. Grainger, K. Healy, D. Hutmacher, and C. J. Kirkpatrick (Elsevier, Oxford, 2017), Chap. 3.6.
[2]D. R. Baer *et al.*, J. Vac. Sci. Technol. A **31**, 050820 (2013).
[3]K. W. Lem, A. Choudhury, A. A. Lakhani, P. Kuyate, J. R. Haw, D. S. Lee, Z. Iqbal, and C. J. Brumlik, Recent Pat. Nanotechnol. **6**, 60 (2012).
[4]P. Linkov, M. Artemyev, A. E. Efimov, and I. Nabiev, Nanoscale **5**, 8781 (2013).
[5]D. R. Baer *et al.*, J. Vac. Sci. Technol. A **37**, 031401 (2019).
[6]Guidance for industry considering whether an FDA-regulated product involves the application of nanotechnology, U.S. Food and Drug Administration, 2014, see https://www.fda.gov/media/88423/download.
[7]C. F. Jones, D. G. Castner, and D. W. Grainger, "Surface adsorbates on nanomaterials and their possible roles in host inflammatory and toxicological processing," in *Handbook of Immunological Properties of Engineered Nanomaterials*, edited by M. A. Dobrovolskaia and S. E. McNeil (World Scientific, Hackensack, NJ, 2013).
[8]A. S. Karakoti, L. L. Hench, and S. Seal, JOM **58**, 77 (2006).
[9]D. W. Grainger and D. G. Castner, Adv. Mater. **20**, 867 (2008).
[10]D. R. Baer, Front. Chem. **6**, 145 (2018).
[11]R. L. Marchese Robinson *et al.*, Nanoscale **8**, 9919 (2016).
[12]B. Pelaz *et al.*, ACS Nano **6**, 8468 (2012).
[13]E. M. Hotze, T. Phenrat, and G. V. Lowry, J. Environ. Qual. **39**, 1909 (2010).
[14]J. M. Pettibone, J. Gigault, and V. A. Hackley, ACS Nano **7**, 2491 (2013).
[15]E. K. Richman and J. E. Hutchison, ACS Nano **3**, 2441 (2009).
[16]D. R. Baer and M. H. Engelhard, J. Electron Spectrosc. **178-179**, 415 (2010).
[17]L.-K. Mireles, E. Sacher, L. H. Yahia, S. Laurent, and D. Stanicki, Data Brief **7**, 1296 (2016).
[18]C. J. Powell, W. S. M. Werner, H. Kalbe, A. G. Shard, and D. G. Castner, J. Phys. Chem. C **122**, 4073 (2018).
[19]N. A. Belsey, A. G. Shard, and C. Minelli, Biointerphases **10**, 019012 (2015).
[20]A. G. Shard, J. Phys. Chem. C **116**, 16806 (2012).
[21]R. França, X. F. Zhang, T. Veres, L. H. Yahia, and E. Sacher, J. Colloid Interface Sci. **389**, 292 (2013).
[22]D. J. H. Cant, Y.-C. Wang, D. G. Castner, and A. G. Shard, Surf. Interface Anal. **48**, 274 (2016).
[23]R. M. Crist, J. H. Grossman, A. K. Patri, S. T. Stern, M. A. Dobrovolskaia, P. P. Adiseshaiah, J. D. Clogston, and S. E. McNeil, Integr. Biol. **5**, 66 (2013).
[24]A. S. Karakoti *et al.*, Surf. Interface Anal. **44**, 882 (2012).
[25]D. R. Baer *et al.*, Surf. Interface Anal. **40**, 529 (2008).
[26]S. V. N. T. Kuchibhatla, A. S. Karakoti, D. R. Baer, S. Samudrala, M. H. Engelhard, J. E. Amonette, S. Thevuthasan, and S. Seal, J. Phys. Chem. C **116**, 14108 (2012).
[27]D. R. Baer, A. S. Karakoti, C. A. Clifford, C. Minelli, and W. E. S. Unger, Surf. Interface Anal. **50**, 902 (2018).
[28]D. R. Baer, P. Munusamy, and B. D. Thrall, Biointerphases **11**, 04B401 (2016).
[29]ISO Standard, *20579-4, Surface Chemical Analysis—Guidelines to Sample Handling, Preparation and Mounting—Part 4—Reporting Information Related to the History, Handling and Mounting of Nano-Objects Prior to Surface Analysis* (ISO, Geneva, 2018).
[30]D. R. Baer, D. J. H. Cant, D. G. Castner, G. Ceccone, M. H. Engelhard, and A. S. Karakoti, "Preparation of nanoparticles for surface analysis," in *Characterization of Nanoparticles Measurement Procedures for Nanoparticles*, edited by W. E. S. Unger, A. G. Shard, and V.-D. Hodoroaba (Elsevier, Oxford, 2019), Chap. 4.2.
[31]W. S. M. Werner, M. Chudzicki, W. Smekal, and J. C. Powell, Appl. Phys. Lett. **104**, 243106 (2014).
[32]S. D. Techane, D. R. Baer, and D. G. Castner, Anal. Chem. **83**, 6704 (2011).
[33]S. D. Techane, L. J. Gamble, and D. G. Castner, J. Phys. Chem. C **115**, 9432 (2011).
[34]M. D. Torelli, R. A. Putans, Y. Tan, and S. E. Lohse, ACS Appl. Mat. Interfaces **7**, 1720 (2015).
[35]S. F. Sweeney, G. H. Woehrle, and J. E. Hutchison, J. Am. Chem. Soc. **128**, 3190 (2006).
[36]R. La Spina, V. Spampinato, D. Gilliland, I. Ojea-Jimenez, and G. Ceccone, Biointerphases **12**, 031003 (2017).
[37]Y.-C. Wang, M. H. Engelhard, D. R. Baer, and D. G. Castner, Anal. Chem. **88**, 3917 (2016).
[38]J. T. Nurmi, V. Sarathy, P. T. Tratnyek, D. R. Baer, J. E. Amonette, and A. Karkamkar, J. Nanoparticle Res. **13**, 1937 (2010).
[39]W. Kern, J. Electrochem. Soc. **137**, 1887 (1990).
[40]S. D. Techane, L. J. Gamble, and D. G. Castner, Biointerphases **6**, 98 (2011).
[41]N. A. Belsey *et al.*, J. Phys. Chem. C **120**, 24070 (2016).
[42]Spin coating: A guide to theory and techniques, Ossila, 2017, see https://www.ossila.com/pages/spin-coating#spin-coating-nanoparticles (last accessed February 2020).
[43]C. Kan-Sen, H. Kuo-Cheng, and L. Hsien-Hsuen, Nanotechnology **16**, 779 (2005).
[44]H. R. Barzegar, F. Nitze, T. Sharifi, M. Ramstedt, C. W. Tai, A. Malolepszy, L. Stobinski, and T. Wågberg, J. Phys. Chem. C **116**, 12232 (2012).
[45]K. Hellgardt and D. Chadwick, Rev. Sci. Instrum. **67**, 4025 (1996).
[46]E. Lochner, *CMMP X-Ray Photo-Electron Spectroscopy* [Condensed Matter and Materials Physics (CMMP) group at Florida State University, Tallahassee, FL, 2013], see http://xps-cmmp.blogspot.com/2013/08/mounting-powder-samples-for-xps.html (last accessed February 2020).
[47]ISO Standard 18117, *Surface Chemical Analysis—Handling of Specimens Prior to Analysis (ISO, Geneva 2009). Also ASTM E1829-14 Standard Guide for Handling Specimens Prior to Surface Analysis* (ASTM, West Conshohocken, PA, 2014).
[48]D. Q. Yang, M. Meunier, and E. Sacher, Appl. Surf. Sci. **173**, 134 (2001).
[49]M. Y. Smirnov, A. V. Kalinkin, A. V. Bukhtiyarov, I. P. Prosvirin, and V. I. Bukhtiyarov, J. Phys. Chem. C **120**, 10419 (2016).
[50]G. Zorn, S. R. Dave, X. Gao, and D. G. Castner, Anal. Chem. **83**, 866 (2011).
[51]A. Frydman, D. G. Castner, M. Schmal, and C. T. Campbell, J. Catal. **152**, 164 (1995).
[52]A. Frydman, D. G. Castner, M. Schmal, and C. T. Campbell, J. Catal. **157**, 133 (1995).
[53]C. Dablemont, P. Lang, C. Mangeney, J.-Y. Piquemal, V. Petkov, F. Herbst, and G. Viau, Langmuir **24**, 5832 (2008).
[54]D. R. Baer, D. J. Gaspar, P. Nachimuthu, S. D. Techane, and D. G. Castner, Anal. Bioanal. Chem. **396**, 983 (2010).
[55]A. Müller *et al.*, J. Phys. Chem. C **123**, 29765 (2019).
[56]C. J. Powell, Micros. Today **24**, 16 (2016).
[57]D. R. Baer, Y.-C. Wang, and D. G. Castner, Micros. Today **24**, 40 (2016).
[58]M. Chudzicki, S. M. W. Werner, A. G. Shard, Y.-C. Wang, D. G. Castner, and C. J. Powell, J. Phys. Chem. C **119**, 2484 (2015).
[59]A. G. Shard, J. Wang, and S. J. Spencer, Surf. Interface Anal. **41**, 541 (2009).
[60]C. J. Powell, W. S. M. Werner, A. G. Shard, and D. G. Castner, J. Phys. Chem. C **120**, 22730 (2016).
[61]W. S. M. Werner, W. Smekal, and C. J. Powell, *NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA), Version 2.1.1, Standard Reference Data Program Database 100* (U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD, 2018), see http://www.nist.gov/srd/nist100.htm.
[62]W. Smekal, W. S. M. Werner, and C. J. Powell, Surf. Interface Anal. **37**, 1059 (2005).
[63]S. R. Sahoo, P. V. R. K. Ramacharyulu, and S.-C. Ke, Anal. Chem. **90**, 1621 (2018).
[64]M. H. Engelhard, J. N. Smith, and D. R. Baer, Surf. Sci. Spectra **23**, 29 (2016).
[65]S. Tougaard, Software packages to characterize surface nano-structures by analysis of electron spectra (QUASES), see http://www.quases.com/products/quases-tougaard/ (last accessed February 2020).