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Evaluating the Internal Structure of Core-Shell Nanoparticles Using X-ray Photoelectron Intensities and Simulated Spectra

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Abstract

The functionality of a new version of the National Institute of Standards and Technology database Simulation of Electron Spectra for Surface Analysis (SESSA) has been extended by implementing a new geometry engine. The engine enables users to simulate Auger-electron spectra and X-ray photoelectron spectra for different predefined morphologies (planar, islands, spheres, multi-layer core-shell particles). We compared shell thicknesses of core-shell nanoparticles derived from core-shell XPS peak intensities using Shard's method, which allows one to estimate shell thicknesses of core-shell nanoparticles, and a series of SESSA simulations for a wide range of nanoparticle dimensions. We obtained very good agreement of the shell thicknesses for cases where elastic scattering within the shell can be neglected, a result that is in accordance with the underlying assumptions of the Shard model. If elastic-scattering effects are important, there can be thickness uncertainties of up to 25 %.

Experimental spectra of functionalized gold nanoparticles obtained by Techane *et al.* were analyzed with SESSA 2.0 both with respect to the relevant peak intensities as well as the spectral shape. Good agreement between experiment and theory was found for both cases. These results show that the single-sphere model for core-shell nanoparticles is valid when just using peak intensities, but more detailed modeling is needed to describe the inelastic background.

Graphical abstract

Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful tool extensively used in surface analysis to study the chemical and physical properties of surfaces and interfaces.^{1–5} As the field of nanotechnology has grown, increasingly engineered and functional nanomaterials are being synthesised and exploited in numerous applications, ranging from biomedical assays to optoelectronic devices. There is a consequent requirement to develop and refine procedures to precisely characterize nanostructures at the nanoscale.^{5–11} XPS is in this regard a very powerful technique as it provides information not only on the composition but also on the chemistry, structure and size of the investigated system.^{12–17}

The physical processes governing the electron-solid interaction in conventional XPS give rise to attenuation of electrons over distances of a few nanometers, which makes XPS suitable for the characterization of nanosized structures.¹⁸ Thus, the signal will be affected by the morphology of the sample, which is a well known fact since the early days of XPS when it was already used to study nanosized catalysts.^{19–21} However, it is far from trivial to extract structural information from XPS spectra. Deriving universal, analytical expressions that directly connect the morphology of a system to peak intensities, or other features of an XPS spectrum, is a formidable task and can often only be achieved by applying various approximations for some special cases.^{22–27} An example of such a direct translation of features of an XPS spectrum to morphological properties is provided by Shard,²⁸ who established a non-iterative, empirical algorithm to estimate the shell thickness of core-shell (CS) particles given the radius of the inner core, the attenuation lengths for photoelectrons in the overlayer and core materials, and the experimental XPS CS peak-intensity ratio.

Alternatively, the QUASES software package can be useful for nanomorphology characterization by essentially comparing background subtracted spectra with a reference spectrum.²⁹ However, at present this is only possible for a limited number of pre-selected morphologies, similar to the earlier versions of SESSA.

In the general case of arbitrary nanostructures for which universal models are presently not available, the process of data interpretation is greatly facilitated by simulation software such as the National Institute of Standards and Technology database for the Simulation of Electron Spectra for Surface Analysis (SESSA), which can be used to simulate XPS spectra and peak intensities for samples with different nanomorphologies.^{30,31} Moreover, employing simulation software provides insight by varying the parameters describing the nanomorphology and matching to features of experimental spectra. SESSA provides all physical quantities required to conduct simulations of Auger-electron- or XPS-spectra for a

given sample using a highly efficient simulation engine operating in the reverse trajectory mode.³² Simulations can be made for any photon energy below 30keV and for any mixture of circularly and linearly polarized light, as defined by a user.

The original version of SESSA provided the capability to simulate spectra for layered specimens with each layer having a given composition and thickness. The present version 2.0 of SESSA provides the capability for simulating spectra for various types of nanomorphologies (spheres, layered spheres and islands). In SESSA 2.0, the geometrical parts of the simulation are performed by the PENGEO package, which constitutes a stand-alone package, distributed within the PENELOPE code system, for defining arbitrary morphologies and tracking of electron trajectories.³³

In a recent work,³⁴ a developmental version of SESSA was used to investigate various systems of nanoparticles (NPs): periodically aligned monolayers of CS particles, dispersed sub-monolayer arrays, as well as powder-like assemblies of CS particles. This work provided information on various features in angle-resolved XPS that arise with increasing periodicity of the investigated structures. Also, it was shown that dispersed powders (i.e. structures without long-range periodicity) of CS particles can be modeled by a single sphere.³⁴

Shard has described a simple method for calculating the shell thickness of CS nanoparticles (NPs),²⁸ which shall be referred to as the “ $T(NP)$ formula” within the present work. This method is based on the straight-line approximation (SLA), in which all signal electrons are assumed to follow rectilinear paths. This approach is a good approximation for materials with small atomic numbers where elastic-scattering effects can often be neglected.

We have used SESSA 2.0 to reproduce results from the $T(NP)$ formula under the same experimental conditions and assumptions for two important cases: a beryllium shell on a gold core and a palladium shell on an aluminum oxide core. The former case (beryllium with atomic number $Z = 4$) is a reasonable model system for a hydrocarbon layer, containing carbon ($Z = 6$) and hydrogen ($Z = 1$), while the latter case is a representation of a catalytic system. Such systems of strong scatterers on weak scatterers and vice versa often appear in nanotechnology in the form of catalysts or functionalized NPs, respectively. The simulations were repeated subsequently under physically more realistic conditions (e.g., taking into account elastic scattering and including contamination layers) to study the limitations of the $T(NP)$ formula.

Techane *et al.*¹⁴ have used SESSA Version 1.3 to simulate CS NPs made of a gold core with an organic shell, a self-assembled monolayer (SAM) of carboxylic acid thiol. As this version did not provide means to simulate spherical particles of any kind, Techane *et al.* modeled a CS nanoparticle (NP) by assembling it from a number of concentric cylinders. The process involved tedious modeling and is therefore not feasible for routine simulations. We have used SESSA Version 2.0 to model spherical, self-assembled monolayers (SAMs) attached to gold NPs. The new software provides a major improvement in terms of speed, efficiency and simplicity compared to the approach of Techane *et al.* with SESSA Version 1.3. The present analysis not only confirms the results of Techane *et al.*¹⁴ but also gives excellent

agreement for the shape of the inelastic background in survey XPS spectra after a transmission-function correction.

Materials and methods

SESSA

SESSA is a standard reference database distributed by the National Institute of Standards and Technology containing all data needed for quantitative simulations of XPS and Auger-electron spectra.^{30,31} Data retrieval is based on a powerful expert system that queries the databases and provides the data to the user or the simulation engine for arbitrarily shaped geometrical configurations. The simulation engine is a particularly crucial part of SESSA as it enables the user to conduct batch simulations of arbitrarily shaped nanostructures.

The extensive capabilities of SESSA Version 2.0 for simulating various nanomorphologies are based on the PENGEOm package, a general-purpose geometry package that allows one to define quasi-arbitrary geometries using quadric surfaces. PENGEOm comes as a standalone part of the PENELOPE code system which is widely used for simulation of electron and photon transport processes.³³ Based on the information provided by the user, a geometry file is created by SESSA and internally passed to PENGEOm which initializes the geometry, stores it in memory and provides various functions for tracking the electron trajectory. The geometry definition is based on a simple syntax with which surfaces such as planes, spheres, hyperboloids etc. can be defined and subsequently used to delimit phases of a material. Existing phases can be further used as building blocks for larger structures.

The recently released version V2.0 does not yet provide the option to load externally defined geometry files; however, this feature will be implemented in the upcoming version V2.1. The possibility to simulate externally defined geometries further expands SESSA's application possibilities as it, for example, enables the simulation of XPS intensities of lithographically manufactured by XPS with hard X-rays. Currently the following morphologies are predefined and can be chosen: planar, roughness, islands, spheres and layered spheres. The planar and roughness morphologies are comprised of an arbitrary number of stratified layers placed on a semi-infinite substrate. The composition and thickness of each layer can be easily changed by the user and SESSA always provides estimates for all needed material properties. For the roughness morphology, an additional parameter is defined to account for the increase in relative surface area (RSA) of a rough surface compared to a perfectly planar specimen. The increase in signal intensity due to an increased surface area is accounted for with the RSA parameter. The island and sphere morphologies enable one to simulate structures placed on a layered sample as in the case of a planar morphology.

For islands, the simulated structure consists of a trapezoid with variable dimensions in x, y and z directions together with variable inclinations of the side-walls. In the case of spheres, the dimensions of the sphere and its composition can be varied. The layered-spheres morphology allows one to simulate a spherical particle consisting of an inner core with an arbitrary number of overlayers. The dimensions of the sphere as well as the composition and thickness of each layer can be chosen by the user. All nanomorphologies are simulated as

periodic arrays where the periods can be selected to represent isolated or dense assemblies of features. As shown in our prior work³⁴ and by Frydman *et al.*,²⁷ the surface of a dispersed powder of CS NP seen by a detector is equivalent to the surface of a single sphere and is independent of the viewing angle by the detector. Therefore, a simulation for a well-dispersed array of CS NPs yields the same ratio of photoelectron intensities from the core and the shell as from a bulk powder.

In order to minimize computation times and to enable faster processing of batch jobs, a highly efficient Monte Carlo code is employed, based on the trajectory-reversal method of Gries and Werner.³² In contrast to conventional Monte Carlo codes where electrons are tracked on their trajectories from the source to the detector, the trajectory-reversal approach tracks electrons in the opposite direction, starting from the detector and following the trajectory back to the point of origin. Thus, all electrons contribute to the signal resulting in significantly decreased simulation times, typically in the range from seconds to several minutes, depending on the number of peaks to be simulated and the desired precision in the results.

Shard's $T(NP)$ formula

Shard²⁸ addressed the general problem of interpretation of XPS intensities of CS particles by establishing a simple and non-iterative procedure, the $T(NP)$ formula, that enables one to directly convert peak-intensity ratios to shell thicknesses in two-component systems. Emphasis was put on CS particles as they constitute a particularly important field of research due to their many applications.^{9,35–39}

The parameters in the $T(NP)$ formula are A , the ratio of the normalized XPS peak intensities from the shell and core materials, respectively, the radius R of the core, and the electron attenuation lengths L of the core and shell photoelectrons in each material. For normalization of the peak intensities I_i , calculated or experimentally determined intensities of the pure materials can be used and are written as I_i^∞ . Following the notation in Shard's work, the subscript $i = 1, 2$ is used to identify photoelectrons arising from the shell and core materials, respectively, giving the normalized peak-intensity ratio A as:

$$A = \frac{I_1 I_2^\infty}{I_2 I_1^\infty} \quad (1)$$

Shard's approach for obtaining an expression for the shell thickness of a CS NP was to make approximations for overlayer thicknesses of different limiting cases, such as planar samples, infinitesimally small particles (see eq. (4)), or macroscopic particles (see eq. (3)). The formula for calculation of nanoscopic CS particles was obtained by combining these limiting cases. The fit parameters a and β were determined by validating the results with numerical calculations, so that the validity of the resulting formula is ensured within the limits of the model and the relevant core radii and shell thicknesses. The resulting $T(NP)$ formula is given by:

$$T_{\text{NP}}(A) = \frac{\frac{T_{R \rightarrow \infty} R}{R + \alpha} + \beta T_0}{1 + \beta} \quad (2)$$

$$T_{R \rightarrow \infty} = \frac{0.74A^{3.6} \ln(A) B^{-0.9} + 4.2AB^{-0.41}}{A^{3.6} + 8.9} \quad (3)$$

$$T_0 = R \left[(ABC + 1)^{1/3} - 1 \right] \quad (4)$$

For a detailed explanation of the values α , β , B and C , the reader is referred to Shard's original work.²⁸

Equation (2) enables one to calculate the shell thickness of a CS NP given the (experimental) normalized intensity ratio, the attenuations lengths L_{ij} of the core and shell materials, as well as the core radius. Both the attenuation lengths and the pure elemental intensities I_i^∞ needed to calculate the normalized intensity ratio A are easily retrieved using SESSA by running simulations or querying the expert system. Equation (2) applies to radii of NPs ranging from approximately 1 nm to 1 μm and provides shell thicknesses with a typical standard uncertainty of 4 %. This uncertainty is considerably smaller than the typical uncertainty of the attenuation lengths L_{ij} , that are based on inelastic mean free paths with estimated uncertainties of about 10 %⁴⁰

Evaluation of the $T(\text{NP})$ formula

In order to evaluate the $T(\text{NP})$ formula, the following approach was adopted: For a given shell thickness, T_{SESSA} , core radius R , and material composition of the CS system, a simulation was conducted using SESSA, yielding a simulated value for the normalized intensity ratio, A_{SESSA} . Using this value for A_{SESSA} in eq. (2), together with the core radius R and the constants B and C , the calculated shell thickness T_{NP} is obtained. In the ideal case T_{SESSA} and T_{NP} are equal, and a plot of T_{SESSA} as a function of T_{NP} yields a straight line with unity slope through the origin.

The $T(\text{NP})$ formula was used to investigate the two previously described model systems consisting of a weakly scattering beryllium shell on a gold core (system 1) and a palladium shell on an aluminum oxide core (system 2), respectively. The evaluation was conducted for four different core radii as displayed in figure 1. For each case, 50 simulations were conducted with varying shell thicknesses in the range from 0.1 $L_{1,a}$ to 5 $L_{1,a}$ in steps of 0.1 $L_{1,a}$.

The values of $L_{1,a}$ for systems 1 and 2 were 3.15 nm and 1.20 nm, respectively. $L_{1,a}$ also determines the size of the simulated CS NPs as T and R are given in units of $L_{1,a}$. Since the overlayer thickness was varied table 1 displays the size ranges of the simulated CS systems. Figure 1 displays the four different CS particle systems used in the simulations. The figure is given to scale to emphasize the wide range of radii employed for the evaluation. The corresponding sizes for each material composition can be found in table 1. It is important to

note that with a shell thickness of $5 L_{1,a}$, the XPS intensity from the core will almost certainly be too weak to measure in practice. For this reason the $T(\text{NP})$ formula was only validated using the SLA up to $\approx 3L_{1,a}$ in the original work²⁸ but, because the formulation is accurate in at least some of the extremes of core radii and shell thicknesses, we may expect it to be valid over a wider range.

Results and Discussion

Evaluation of the $T(\text{NP})$ formula

Figure 2 displays the results of the evaluation in form of a plot displaying T_{NP} against T_{SESSA} for the Be/Au and Pd/Al₂O₃ CS NPs for cases **I**, **II**, **III** and **IV** of figure 1 and the range of shell thicknesses described above. The red dotted lines consist of 50 discrete points each corresponding to an independent simulation. Two sets of simulations were performed for each set of materials, core radii, and shell thicknesses, one accounting for elastic-scattering effects (b and d) and one with the SLA (a and c) where all electron trajectories follow rectilinear paths. Values of T_{SESSA} and T_{NP} were normalized to the appropriate value of $L_{1,a}$.

As seen on the left side of figure 2, few significant deviations occurred between T_{NP} and T_{SESSA} for the Be/Au system, both when elastic scattering was accounted for and when the SLA was employed since the shell is a weakly scattering material. That is, most trajectories are close to rectilinear.

It should be stressed that the $T(\text{NP})$ formula is based on the SLA and does not account for elastic scattering. For the Be/Au model system, there is generally good correlation between T_{NP} and T_{SESSA} . Some small deviations, however, were found at relatively large shell thicknesses ($T/L_{1,a} \approx 3$) and a core radius of $R = 0.5 L_{1,a}$, as shown in panel **IVa** in figure 2. The deviations, however, appear at shell thicknesses which are beyond the limits of the $T(\text{NP})$ formula, which was established for shell thicknesses of approximately $T/L_{1,a} \approx 3$.²⁸

For Pd/Al₂O₃ NPs the shell material has a high atomic number and stronger elastic-scattering effects are expected.¹

Elastic scattering leads to deflections of photoelectrons emitted from the core material and therefore a lower core signal, thus resulting in an overestimate of the shell thickness using the $T(\text{NP})$ formula. A comparison between results of simulations conducted with and without the SLA in figure 2 shows this effect very convincingly.

The simulations denoted by **Ic** to **IVc** were carried out using the SLA and in this case there are no significant differences between T_{NP} and T_{SESSA} . The deviations from this ideal behavior due to elastic-scattering effects manifest themselves very clearly in the **Id** to **IVd** panels.

This effect can be explained by comparing the relative contributions of core and shell photoelectrons of two CS NPs with different radii but constant shell thickness, as shown in figure 1–I and 1–IV. For a very small core radius, the whole core contributes to the signal in equal measure. Also, the relative shell intensity is then much larger as the shell comprises

most of the CS particle volume. However, given a large core radius with the same shell thickness, most of the core intensity originates from the region just beneath the shell. As a first approximation, the relative volume ratio of the core and shell regions contributing to the signal and the normalized intensity ratio A are both closer to unity than in the former case. The attenuation of the core signal due to elastic scattering has a larger impact on larger particles as the signal contribution from the core increases. This behavior is also reflected in eq. (3), which has a logarithmic contribution in A . The value of A , giving the shell-to-core ratio of photoelectron intensities, is large for small particles where the shell is dominant. Since the shell-to-core ratio A has a logarithmic contribution to the $T(\text{NP})$ formula, as seen in equation (2) and equation (3), the uncertainty in the calculated shell thickness will be large for small values of A , while for large values of A the uncertainty will be negligible. Thus, when A is close to unity, small changes in A have a large effect on its logarithm, leading to deviations at smaller shell thicknesses.

The Pd/Al₂O₃ material system was also studied with regard to the influence of a 0.15 nm carbonaceous contamination layer on the normalized intensity ratio and the predicted shell thickness. It was found that the results obtained with and without the thin contamination layer were indistinguishable for all cases, meaning that the presence of a thin carbonaceous contamination layer does not affect the result obtained with the $T(\text{NP})$ formula, given that the contamination is the only carbonaceous compound of the CS system. Thicker contamination layers, which approach the electron attenuation length in thickness, will affect the accuracy of the $T(\text{NP})$ calculation. Such situations can be classed under the general case of core-shell-shell systems. These may be easily modelled using SESSA but significant modifications to the $T(\text{NP})$ approach are required to deal with such systems. As shown later in fig 3, such a contamination layer has a large influence on the normalized intensity ratio if carbon is present within the core or shell.

In summary the $T(\text{NP})$ formula performs very well on systems where applying the SLA is justified, such as gold NPs functionalized with alkanethiols. However, the method has relatively large uncertainties (up to 25 % in panels **Id** to **IVd** of figure 2) in the shell thicknesses of material systems comprised of a strongly scattering shell since the $T(\text{NP})$ formula is based upon the assumption of rectilinear electron trajectories.

Application of SESSA to experimental XPS data

Self-assembled monolayers (SAMs) of alkanethiols on flat gold surfaces are a widely employed model system in nanotechnology due to their well-defined structure and surface properties. Numerous studies deal with the synthesis, characterization, thermodynamics, and reactivity of alkanethiols on flat gold surfaces but there are still many open questions regarding basic properties of SAMs on highly curved surfaces.^{35,41–46}

Techane *et al.*¹⁴ conducted a quantitative analysis of the SAM-layer thickness of 16-mercaptohexadecanoic acid (C₁₆COOH) on flat gold and on 14nm diameter gold nanospheres using XPS for experimental measurements and SESSA Version 1.3 for simulations of the two systems. Since SESSA 1.3 did not provide means to simulate spherical particles directly, Techane *et al.* modeled a CS particle using nine concentric cylinders connected by flat, angled surfaces. These top surfaces, consisting of C₁₆COOH

overlayers attached to a semi-infinite gold substrate were simulated using SESSA 1.3. In order to get the correct peak intensities of the SAM on a gold NP, geometric weighting factors were applied to each simulated surface to account for the different areas.

With SESSA Version 2.0, simulation of CS NPs with an arbitrary number of shells becomes a matter of defining the compositions, thicknesses, and atomic densities of each layer with the help of a user-friendly graphical user interface. The simplicity of this approach enables users without detailed expertise in modeling to investigate systems of different nanomorphologies on a routine basis. In the present work, SESSA 2.0 was employed to model the data of Techane *et al.*

Simulation of SAMs with SESSA 2.0

Unlike a dense material, the atomic density of SAMs attached to highly curved surfaces decreases with the radius because of the spreading of the aliphatic chains. It should be noted that, on an atomic scale, gold NPs consist of (111) and (100) terraces and are therefore not perfectly spherical;^{11,47} however, in the course of this work the 14nm gold NPs were assumed to be perfectly spherical to facilitate the process of simulation with SESSA.

In Techane's model, the atomic density was assumed to be constant throughout the whole thickness of each concentric cylinder, since accounting for the changing density was not easily possible using their approach.¹⁴ A decreased SAM density with radius of the gold NP could result in the enhanced mobility of the chains leading to defects and kinks in the structure of the SAM and a reduced thickness compared to the corresponding SAM on a planar substrate.

The goal of the work by Techane *et al.* was to obtain the best possible agreement between the experimentally derived and simulated normalized intensities by varying the thickness of the CH₂ groups and the relative surface area (RSA) parameter. This parameter accounts for the increase in surface area due to curvature or roughness of an/ otherwise planar surface and it was employed by Techane *et al.* as a second parameter to optimize results from their simulations.

In the work of Techane *et al.*, satisfactory agreement between the simulated and experimental data required introduction of a CH₂-contamination layer. The signal contribution originating from this ubiquitous contamination layer significantly adds to the carbon signal from the deeper buried CH₂ shells and was required for good agreement. The impact of the contamination layer on the carbon intensity was studied using SESSA by simply adding or removing an additional hydrocarbon layer on top of the SAM.

We assumed that the gold NPs were perfectly spherical and had a diameter of 14 nm. This choice is based on transmission electron microscopy measurements that gave a size distribution of 14 nm $\pm$ 1.5 nm and a circularity (ratio of the major axis to the minor axis of the particles) of 1.09 $\pm$ 0.06.¹⁴ The surface density of the C₁₆COOH chains was 0.214 nm²/chain,¹⁴ which amounts to approximately 2877 chains attached to the surface of a single 14nm NP. The atomic density within each layer was calculated in a way that, multiplying it by the volume of the shell, gives the total number of atoms occupying the shell, e.g., 2877

sulfur atoms in the innermost shell or 3×2877 atoms in each CH₂ shell. This method ensures that the total number of atoms equals the number of chains times the number of atoms per chain.⁴⁸ The C₁₆COOH chains were assumed to be immobile and perfectly aligned, so that the only degree of freedom is the tilting angle relative to the normal which could affect the effective thickness of the CH₂ groups. Since the total number of atoms attached to a NP is constant, the tilt of the SAM can be imitated by reducing the thickness of the CH₂ shells and accordingly increasing the atomic density within the shells.

Results

Employing the same approach as Techane *et al.*,¹⁴ a number of simulations with different CH₂ thicknesses was conducted to find the thickness that provided the best agreement with experimental XPS data. Figure 3 displays the normalized photoelectron intensities of each element from the SESSA simulation for CH₂ shell thicknesses ranging from 0.08 nm to 0.11 nm/CH₂ group together with the experimental data. We also show results for one case where the simulation was conducted without the hydrocarbon contamination layer in order to study the impact of this layer. There is generally good agreement between the experimental intensities and the simulated intensities when an additional contamination layer was included. The leftmost bar shows the simulated intensities when the hydrocarbon contamination layer was omitted. This omission had a considerable impact on the gold, carbon and oxygen intensities, as they are significantly over- or under-estimated compared to the experiment. Considering the minimal effort to set up and run the simulations, this result shows the capability of SESSA 2.0 in facilitating the simulation of systems composed of NPs. The experimentally determined normalized intensities of the C1s, Au4f, O1s and S2p photoelectron peaks are listed in table 2 and compared with results obtained from SESSA 1.3 and SESSA 2.0 for an emission angle of 0° relative to the surface normal. To find the shell thickness with the best agreement between the experimentally determined atomic compositions %_{i,Experiment} and the simulated compositions %_{i,SESSA}, the sum-of-squares difference, ΣX^2 , shown in eq. (5) was calculated for each case:

$$\sum X^2 = \sum_{i=\text{Au,C,O,S}} (\%_{i,\text{SESSA}} - \%_{i,\text{Experiment}})^2 \quad (5)$$

Figure 4 shows the total value for the sum-of-squares difference ΣX^2 and the contributions to ΣX^2 from each element for each CH₂-thickness shown in figure 3. Based on this figure, it is clear that it is necessary to account for the CH₂ contamination layer to obtain results with satisfactory agreement with the experiment.

Compared with SESSA 1.3, the agreement with the experimental data for the carbon, gold and oxygen intensities is matched. The sulfur peak intensity simulated with SESSA 2.0, however, is slightly outside of the experimentally estimated standard deviation range. Based on the resulting sum-of-squares difference ΣX^2 , displayed on the right side of figure 4, the CH₂-thickness of 0.10 nm and 0.11 nm per CH₂-group and a hydrocarbon contamination layer of 0.15nm give the best agreement with the experiment. This corresponds to a total film thickness of 2.00nm and 2.15nm, respectively, which is close to Techane's result of 1.85nm.

Full spectral comparison between SESSA and experiment

With SESSA it is not only possible to simulate photoelectron peak intensities but also to simulate entire spectra. This feature of the software was used to conduct a full spectrum match between the measured and simulated spectra of the gold NP SAMs. The transmission function of the XPS apparatus used to record the spectra was estimated.

In contrast to all previously discussed cases where only the elastic (i.e. zero-loss) peak intensities were of interest, the inelastic background also needs to be correctly accounted for. As shown in a previous work,³⁴ a single NP is a useful model system for dispersed powders and yields the same elastic-peak intensities. However, the inelastic background obtained from a single NP is significantly different from the inelastic background of a dispersed powder, and a more suitable morphology is needed to reproduce it correctly. Therefore, using external software a PENGEO geometry of an array of dispersed CS particles resembling a powder was created and simulated with SESSA to ensure the correct shape of the inelastic background. However, SESSA assumes a constant transmission function, so in order to compare the experimental and simulated spectra with each other, a transmission-function correction needs to be applied to the experimental data. The transmission function was estimated as follows: First, the normalized intensities of the C1s, O1s and Au4f peaks were determined using the experimental spectra.¹⁴ Then, each atomic composition was normalized to the Au4f peak and divided by the transmission-corrected data provided by Techane *et al.* in the original paper.¹⁴ The sulfur peak was omitted and corrected for since the provided data did not allow us to extract useful data for the minor sulfur peaks. Plotting these elemental ratios for each element gives three points that represent a crude approximation for the transmission function normalized to the Au4f_{7/2} binding energy of 84.0 eV. In order to validate this result, a second approach was adopted where the experimental and the simulated spectra were divided by one another, followed by fitting a second-order polynomial through the ratio data. The derived function is a crude approximation for the transmission function, given that the differences between the experimental and simulated spectra are most likely due to the energy dependence of the transmission function.

Figure 5a shows the simulated and experimental spectra, where the simulation was normalized to the C1s peak of the experiment. When comparing these spectra the simulated spectrum appears to be skewed relative to the experimental spectrum. This skewness can be partially attributed to the transmission function of the XPS instrument used for the experiment.

Correcting the experimental spectrum for the transmission function yields the spectrum shown in figure 5b, which exhibits a nearly ideal agreement with the simulation. Also, as seen in figure 5c, the transmission function obtained by comparing the atomic compositions as well as simply dividing one spectrum by the another yields very similar results.

Having an approximate expression for the transmission makes it possible to directly compare the experimental and simulated spectra. Figure 6 shows experimental spectra for SAMs on gold NPs (figure 6a), SAMs on flat gold (figure 6b), and the corresponding simulated spectra, all normalized to the Au4f peaks. For comparison a simulated spectrum of

a single gold NP (figure 6c) is displayed which exhibits a clearly different background shape.

The transmission-function correction was essentially derived using the experimental data for gold NPs and the corresponding simulation of a powder-like geometry. The same transmission correction was applied to the experimental spectrum for SAMs on flat gold, again leading to good agreement with the simulation. In general, it can be seen that the background shapes are distinguishable and that SESSA V2.0 is capable of correctly reproducing the background shape using an externally loaded PENGEOm geometry file, in contrast to the single-particle model, where only the peak-intensity ratios are correctly reproduced.

Summary and Conclusions

We have substantially improved SESSA by implementing the PENGEOm package that enables one to simulate different predefined nanomorphologies in addition to the previous functionality to simulate planar samples. Using the $T(\text{NP})$ formula, a comparison of simulated and calculated shell thicknesses of CS NPs was made. The results obtained with SESSA 2.0 are in perfect agreement with the $T(\text{NP})$ formula within the limits of the underlying model which is based on the SLA. With SESSA 2.0, it was very easy to study the limits of the $T(\text{NP})$ formula and it was shown that it is highly suitable for determining shell thicknesses of organic materials but overestimates shell thicknesses for CS particles with strongly scattering shells.

SESSA 2.0 was also applied to a further analysis of experimental data (14nm gold particles functionalized with an alkanethiol¹⁴) in which results were previously obtained with SESSA 1.3 and a model in which spherical particles were represented by an array of differently angled surfaces. With the new version of SESSA it was straightforward to allow the radial density to vary. For the total alkanethiol film thickness two values of 2.00nm and 2.15nm were found, which both gave equally good agreement with the experimental data, compared to the previous result of 1.85nm.¹⁴

Furthermore, we have compared experimental spectra for SAMs on flat gold and SAMs on 14nm gold NP¹⁴ with simulations. In order to compare experimental spectra with simulations, it was necessary to correct the simulations for the transmission function of the XPS instrument used to measure the experimental spectra. The corrected simulations exhibited very good agreement with the experimental spectra with regard to the shape of the inelastic background, thus showing that SESSA 2.0 is capable of correctly reproducing not only XPS peak intensities but also XPS spectra of dispersed arrays of CS particles. The spectra for SAMs on flat gold and gold NPs were then compared with the spectrum of a single SAM gold NP, which is a model system often employed in XPS. This comparison was conducted to show the significant differences in the shape of the inelastic background that arise due to the presence of a dispersed array of NPs and which are missing if a single particle is simulated.

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Figure 1.

To scale representation of the four CS systems used for the evaluation of the $T(\text{NP})$ formula. The definition of the core radius R and the shell thickness T are displayed in the bottom left corner. The actual size depends on the chosen shell material as all dimensions are given in units of $L_{1,a}$, the attenuation length of shell photoelectrons within the shell. For both model systems, the values of $L_{1,a}$ are listed at the bottom. In all four cases **I–IV**, the shell thickness T is depicted with a constant thickness of $5 L_{1,a}$ while the simulations were conducted for values ranging from $0.1 L_{1,a}$ to $5 L_{1,a}$. The core radii for cases **I** to **IV** are respectively: **I** $R = 32 L_{1,a}$, **II** $R = 8 L_{1,a}$, **III** $R = L_{1,a}$, **IV**: $R = 0.5 L_{1,a}$.

Figure 2.

T_{NP} plotted against T_{SESSA} for the Be/Au and the Pd/ Al_2O_3 NP systems of figure 1. T_{NP} was calculated according to eq. (2) using the normalized intensity ratio A_{SESSA} obtained from a simulation conducted with the shell thickness T_{SESSA} . Every red dot corresponds to a simulation at a different shell thickness, ranging from $0.1 L_{1,a}$ to $5 L_{1,a}$. For each material system the plots on the left side were conducted with the SLA, whereas the plots on the right side depict simulations with elastic scattering. The roman numerals correspond to the numerals in figure 1.

Figure 3.

Comparison of normalized intensities of the C1s, Au4f, O1s and S2p peaks determined by XPS and simulations conducted for different CH₂ shell thicknesses and the presence and absence of a hydrocarbon surface contamination with SESSA 2.0

Figure 4.

Contributions to the sum-of-squares difference for each case depicted in figure 3 and the total sum-of-squares difference ΣX^2 .

Figure 5.

Experimental, simulated and transmission-corrected spectra of $C_{16}COOH$ SAMs on 14 nm gold NPs at an emission angle of 0° relative to the surface normal and the resultant approximation of the transmission function. **(a)** Comparison of experimental and simulated spectra, both normalized to the C1s peak. Since SESSA does not account for the transmission function of the experimental setup, the spectra do not match. **(b)** Comparison of the transmission-corrected experimental spectrum and the simulated spectrum. By fitting a second-degree polynomial to the transmission function and dividing the experimental

spectrum by this function, very good agreement is obtained with the experimental spectrum.

(c) Display of the transmission function obtained by comparing elemental compositions together with the second-order polynomial fit for the binding-energy range between -800 eV and -150 eV and by dividing the experimental spectrum by the simulated spectrum

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Figure 6.

Comparison of transmission-corrected, experimental data for SAMs on flat gold and SAMs on gold NPs with the corresponding simulations. Also, the simulated spectrum of a single gold NP is shown. The clear difference in background shapes between the flat geometry and the NP is apparent. In contrast, the single gold NP model correctly predicts the peak-intensity ratio but exhibits a significantly different background shape. The subfigures **a**, **b** and **c** are schematic representations of the simulated morphologies; **a**) Powder-like arrangement of CS particles; **b**) a SAM layer located on a gold substrate; **c**) single CS nanoparticle on a infinite substrate

Table 1

Minimum and maximum diameters of the Be/Au and Pd/Al₂O₃ CS NPs for each core radius, according to figure 1. The minimum and maximum values depend on the shell thickness, which ranged from $0.1L_{1,a}$ to $5L_{1,a}$

Core radius R	Be/Au		Pd/Al ₂ O ₃	
	<i>min. diameter [nm]</i>	<i>max. diameter [nm]</i>	<i>min. diameter [nm]</i>	<i>max. diameter [nm]</i>
$0.5 L_{1,a}$	3.79	34.71	1.44	12.23
$1 L_{1,a}$	6.94	37.86	2.65	14.43
$8 L_{1,a}$	51.11	82.03	19.49	31.27
$32 L_{1,a}$	202.55	233.47	77.22	89.01

Table 2

Normalized intensities of the C1s, Au4f, O1s and S2p peaks determined by XPS measurements and simulations with SESSA 1.3¹⁴ and SESSA 2.0 with and without a surface hydrocarbon contamination layer for an emission angle of 0° relative to the surface normal

Photoelectron line	Experiment	Normalized intensities (%)		
		SESSA 1.3 with cont. layer 0.09 nm/CH ₂ group	SESSA 2.0 with cont. layer 0.11nm/CH ₂ group	SESSA 2.0 without cont. layer 0.11nm/CH ₂ group
C1s	64.9 ± 1.1	64.7	65.2	62.9
Au4f	21.6 ± 0.4	21.5	21.8	22.8
O1s	11.4 ± 1.1	11.8	11.6	12.8
S2p	2.1 ± 0.3	1.9	1.5	1.6