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Comparisons of Analytical Approaches for Determining Shell Thicknesses of Core-Shell Nanoparticles by X-ray Photoelectron Spectroscopy

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Abstract

We assessed two approaches for determining shell thicknesses of core-shell nanoparticles (NPs) by X-ray photoelectron spectroscopy (XPS). These assessments were 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. First, we demonstrated the validity of an empirical equation developed by Shard for determinations of shell thicknesses. Values of shell thicknesses from the Shard equation typically agreed with actual shell thicknesses to better than 10 %. Second, we investigated the magnitudes of elastic-scattering effects on photoelectron peak intensities by performing a similar series of simulations with elastic scattering switched off in our simulation software. Our ratios of the C-shell 1s intensity to the Au-core 4f_{7/2} intensity with elastic scattering switched off were qualitatively similar to those obtained by Torelli *et al.* from a model that neglected elastic scattering. With elastic scattering switched on, the C 1s/Au 4f_{7/2} intensity ratios generally changed by less than 10 %, thereby justifying the neglect of elastic scattering in XPS models that are applied to organic ligands on Au-core NPs. Nevertheless, elastic-scattering effects on peak-intensity ratios were generally much stronger for C-core/Au-shell, Al-core/Cu-shell, and Cu-core/Al-shell NPs, and there were second-order dependences on core diameter and shell thickness.

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Notes

The authors declare no competing financial interest.

Supporting Information

Figures S1, S2, and S3 with plots of (a) A_e , the value of the parameter A in the Shard equation when elastic scattering was switched on in the SESSA simulations, and (b) A_{nc} , the value of the parameter A in the Shard equation when elastic scattering was switched off in the SESSA simulations, for C-core/Au shell NPs, Al-core/Cu-shell NPs, and Cu-core/Al-shell NPs, respectively, as a function of core diameter and for selected shell thicknesses between 0.5 nm and 3 nm.

Graphical Abstract

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has been used for many years to characterize nanoparticles (NPs).^{1–24} Early studies focused on supported-catalyst materials to determine particle size, chemical composition, and chemical state, while more recently NPs have been developed for biomedical and other applications that involve unsupported core-shell NPs in complex environments. The recent growth in NP applications has presented new challenges and opportunities for XPS that require the development of new data-analysis methods and experimental protocols.⁴

We consider here two approaches for determining shell thicknesses of core-shell NPs by XPS. First, we extend our earlier evaluation¹⁷ of the Shard⁸ equation for measuring shell thicknesses from ratios of photoelectron intensities from the core and shell materials of the NP. Second, we address a necessary simplification generally made in the development of analytical models describing photoelectron intensities from NPs of different sizes and with different shell thicknesses. To obtain tractable as well as useful solutions, the effects of elastic scattering of the photoelectrons in the NPs have generally been neglected,^{3,6,10,13,19} and we investigate here the effects of this simplification.

We utilized simulated XPS spectra from the National Institute of Standards and Technology (NIST) Database for the Simulation of Electron Spectra for Surface Analysis (SESSA).^{26,27} In our previous analysis of the Shard equation,¹⁷ we made use of simulated spectra for idealized NPs that consisted of Cu in both the core and the shell. This choice was made because elastic-scattering effects for Cu 2p_{3/2} photoelectrons excited by Al K α X-rays are known to be strong²⁸ and it was possible in SESSA to switch elastic-scattering effects on and off. We then showed that use of the effective attenuation length (EAL) for Cu 2p_{3/2} photoelectrons in a Cu film on a planar substrate was valid when elastic-scattering was switched on while the inelastic mean free path (IMFP) of Cu 2p_{3/2} photoelectrons in Cu was

valid when these effects were switched off.¹⁷ This result led us to infer that the Shard equation would be satisfactory for other materials where the magnitudes of elastic-scattering effects were intermediate between those where the effects were negligible (as represented by our Cu result with elastic scattering switched off in SESSA) and where the effects were relatively strong (as represented by our Cu result with elastic scattering switched on in SESSA).

The Shard equation [eq. (1) below] contains three material-specific parameters.⁸ The parameter A is the ratio of the chosen photoelectron intensities from the core and shell materials normalized by the corresponding ratio of these intensities from planar semi-infinite materials. The parameters B and C are ratios of the EAL for photoelectrons from the shell in the shell material to the EAL for core photoelectrons in the shell material and to the EAL for shell photoelectrons in the core material, respectively. Shard optimized his equation so that elastic-scattering effects in core-shell NPs could be represented by EALs obtained from attenuation measurements or calculations for overlayer films on planar substrates. Specifically, EALs developed for describing attenuation of substrate photoelectrons by an overlayer film were recommended for use in the Shard equation.

Our previous evaluation¹⁷ of the Shard equation was performed for Cu-core/Cu-shell NPs and for this idealized case, $B = C = 1$. We will consider here core-shell material combinations with more extreme values of B and C . Shard investigated relative errors in thickness values from his formula for values of B and C between 0.5 and 2, and found that these errors were less than about 6 %. The relative errors were also judged to be satisfactorily small in comparison with the estimated uncertainties of inelastic mean free paths (on which the EALs depend) of ≈ 10 %.²⁹ We report here further evaluations of the Shard equation from SESSA simulations using Au-core/C-shell, C-core/Au-shell, Cu-core/Al-shell, and Al-core/Cu shell NPs. These material combinations were chosen since they led to suitably large or small (B , C) combination values of (0.88, 2.56), (1.13, 0.39), (2.21, 1.49), and (0.46, 0.68), respectively, for our selected photoelectron signals (Au 4f_{7/2}, C 1s, Cu 2p_{3/2}, and Al 2p_{3/2}). While our results for the Au-core/C-shell NPs are directly relevant to many investigations of Au NPs with various organic coatings,^{7,12,13,18,20,21,23–25} the results for Cu-core/Al-shell and Al-core/Cu-shell NPs are illustrative for XPS characterizations of bimetallic core-shell NPs.^{14, 16}

We will also report on evaluations of the effects of elastic scattering on ratios of photoelectron intensities from the core and shell materials of our chosen NPs. These effects have previously been neglected in the development of analytical models for determining shell thicknesses from measured XPS intensities. Finally, we discuss the reliability of XPS in comparison with other methods for determining shell thicknesses of NPs.

MATERIALS AND METHODS

Shard equation

Shard⁸ proposed a series of analytical expressions that can be used to determine the shell thickness of a core-shell NP. The expressions are a parameterization of the results of numerical calculations of XPS intensities from ideally concentric spherical core-shell

particles with a range of different core radii, shell thicknesses, material densities, and electron energies. The numerical calculations were performed under the assumption that the photoelectrons travel in straight lines (i.e., the so-called straight-line approximation (SLA)) and that their attenuation can be described in terms of an exponential decay in intensity with distance travelled through a particular material. There is an additional, implicit assumption that the characteristic length (EAL) associated with the exponential decay is the product of an energy-dependent term and a material-dependent term.

In general, it is necessary to consider four EALs for the two photoelectron energies and the two materials of a core-shell NP. These EALs are represented as $L_{i,j}$, where i represents the material from which the photoelectrons originated ($i = 1$ for the shell material and $i = 2$ for the core material) and j indicates the material through which the photoelectrons are traveling ($j = a$ for the shell and $j = b$ for the core). For example, $L_{1,a}$ represents an EAL for photoelectrons from the shell traveling in the shell. It was convenient in the parameterization to use $L_{1,a}$ as a scaling parameter and to express all quantities with units of length as ratios to this EAL. This procedure enables a simplicity of expression in the final equations. The radius of the NP core is defined as the product $PL_{1,a}$ where P is the dimensionless ratio of the physical radius of the core to $L_{1,a}$. P is one of the inputs into the Shard equation and the dimensionless output, T_{NP} , should be multiplied by $L_{1,a}$ to provide an estimate of the physical thickness of the shell.

The Shard expressions are:

$$T_{NP} = \frac{T_{P-1} + \beta T_0}{1 + \beta}, \quad (1a)$$

where

$$T_{P-1} = \frac{T_{P \rightarrow \infty} P}{P + \alpha}, \quad (1b)$$

$$T_0 = P[(ABC + 1)^{1/3} - 1], \quad (1c)$$

$$T_{P \rightarrow \infty} = \frac{0.74A^{3.6} \ln(A)B^{-0.9} + 4.2AB^{-0.41}}{A^{3.6} + 8.9} \quad (1d)$$

$$\alpha = 1.8/(A^{0.1}B^{0.5}C^{0.4}), \quad (1e)$$

$$\beta = 0.13\alpha^{2.5}/P^{1.5}, \quad (1f)$$

$$A = I_1 I_2^\infty / I_2 I_1^\infty, \quad (1g)$$

$$B = L_{1,a}/L_{2,a}, \quad (1h)$$

and

$$C = L_{1,a}/L_{1,b}. \quad (1i)$$

In eq. (1g), I_1 indicates the photoelectron intensity from the shell and I_2 the photoelectron intensity from the core. The quantities, I_1^∞ and I_2^∞ , represent the corresponding intensities from planar semi-infinite materials. Equations (1h) and (1i) utilize ratios of $L_{1,a}$ to the EALs $L_{2,a}$ and $L_{1,b}$, respectively. Shad assumed that the fourth EAL, $L_{2,b}$, could be estimated from $L_{2,b} = L_{1,a}/BC$. We note that eq. (1d) was shown incorrectly in our previous paper¹⁷ but the numerical results therein are correct.

SESSA

SESSA^{26,27} is a NIST database that can be used to simulate XPS spectra [and also Auger-electron spectra (AES)] of nanostructures such as islands, lines or rods, spheres, and layered spheres on surfaces. Similar simulations can be performed for multilayer films.²⁸ Users can specify the compositions and dimensions of each material in the sample structure as well as the measurement configuration, and the simulated spectra can be compared with measured spectra. Compositions and dimensions can then be adjusted to find maximum consistency between simulated and measured spectra. We point out that comparisons of this type should only be made with measured spectra that have been corrected for the transmission function of the instrument.

The SESSA database has been designed to facilitate quantitative interpretation of AES and XPS spectra and to improve the accuracy of quantitation in routine analysis.^{26,27} SESSA contains physical data needed to perform quantitative interpretation of an AES or XPS spectrum for a specimen of given composition and morphology (differential inverse inelastic mean free paths, total inelastic mean free paths, differential elastic-scattering cross sections, total elastic-scattering cross sections, transport cross sections, photoionization cross sections, photoionization asymmetry parameters, electron-impact ionization cross sections, photoelectron lineshapes, AES lineshapes, fluorescence yields, and Auger-electron backscattering factors). Retrieval of relevant data is performed by a powerful expert system

that queries the comprehensive databases. A simulation module provides an estimate of individual peak intensities. These peak intensities are provided directly, i.e., without any need for selection of and then subtraction of a background intensity.

The Shard equation, eq. (1), is an empirical approach based on the SLA and provides a very simple and fast method for calculating shell thicknesses of core-shell NPs. SESSA models the physical processes of electron transport by performing statistical simulations of photoelectron trajectories.²⁷ The most crucial input parameters for such simulations are the IMFPs and the elastic-scattering cross sections (when elastic scattering is to be accounted for) for each material and each kinetic energy. From the trajectory simulations, the ratio of the peak intensities for particular shell and core materials of a NP [eq. (1g)] can be calculated as a function of a selected core radius, P , and the selected shell thickness, T . Since eq. (1g) also involves ratios of the corresponding peak intensities from planar samples, the resulting values of A are less sensitive to uncertainties in the absolute values of the IMFPs and elastic-scattering cross sections for each material.²⁹

For some shell materials, such as organic compounds, it is commonly assumed that elastic scattering does not have a significant impact on the measured intensity ratios. In such cases, SESSA simulations with elastic-scattering effects included and neglected (the SLA) are expected to yield almost identical results. Furthermore, the IMFP and the EAL are also identical when elastic-scattering effects are small, and the SLA is a useful simplification. In other cases, by accounting for elastic-scattering effects, SESSA provides more realistic results in exchange for significantly greater complexity. The magnitudes of elastic-scattering effects on values of A are reported here for our selected NP core-shell materials.

The design of the SESSA software allows the user to enter the required information in an intuitive way. The modular structure of the user interface closely matches that of the usual controls on a real instrument. A command line interface can also control the software; this feature allows users to load sequences of commands that facilitate a series of simulations for similar conditions (i.e., batch runs).

The capabilities of the present SESSA Version 2.1 for simulating XPS spectra of samples consisting of selected nanomorphologies on a planar substrate are based on the PENGEO package, a general-purpose geometry package that allows one to define quasi-arbitrary sample structures using quadric surfaces.³⁰ PENGEO is a part of the PENELOPE code which is widely used for simulation of electron and photon transport in matter.³¹ From information provided by a user, a geometry file is created by SESSA and internally passed to PENGEO which initializes the geometry, stores it in memory, and provides various functions for tracking an electron trajectory. The geometry 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.

The layered-sphere morphology in SESSA allows simulations for a spherical particle (the core) with an arbitrary number of “overlayer” shells. In our work, there was a single concentric shell. Our simulations were performed with Au-core/C-shell, C-core/Au-shell, Al-core/Cu-shell, and Cu-core/Al-shell NPs. We chose the low-density form of carbon

(“glassy C”) with a density of 1.8 g/cm^3 that would be a better representation of organic materials than graphite or diamond. We selected core diameters, D , of 1 nm, 2 nm, 5 nm, 10 nm, 20 nm, 50 nm, 100 nm, and 200 nm, and we varied the shell thicknesses, T , between 0.25 nm and 3 nm in increments of 0.25 nm. Each simulation was performed with SESSA 2.1 options that allow for a *single* core-shell NP (with selected materials and dimensions) and *without* a substrate. These choices allowed much faster simulations.

The simulations were performed with Al K α X-rays incident on the NP at an angle of 55° with respect to the analyzer direction, and we determined intensities of photoelectrons that were emitted within 5° of the surface normal. For each chosen core-shell material combination and dimensions, simulations were performed with elastic scattering switched on and with elastic scattering switched off.

The Monte Carlo simulations in SESSA are based on the trajectory-reversal approach of Gries and Werner.³² In contrast to conventional Monte Carlo codes in which electrons are tracked from the source to the detector, the trajectory-reversal method tracks electrons in the opposite direction, starting from the detector and following a trajectory back to the point of origin. All electrons thus contribute to the accumulated signal which results in significantly shorter simulation times. Our simulations typically took about 10 seconds on a personal computer. We note that SESSA does not now take account of possible variations in the fraction of intrinsic or shakeup intensity accompanying photoionization with film thickness or photoelectron emission angle and/or to possible variations in the inelastic-scattering probabilities in the vicinity of surfaces and interfaces, again as a function of film thickness or photoelectron emission angle. SESSA also does not take into account IMFP variations with energy in the simulation of a photoelectron spectrum. Nevertheless, we find satisfactory agreement between simulated spectra and measured spectra in comparisons over energy regions of about 100 eV below a photoelectron peak.^{33,34}

IMFP and EAL Data

IMFPs for Al, Cu, and Au were obtained from data published by Tanuma *et al.*³⁵ while IMFPs for glassy C were obtained from the predictive IMFP formula designated TPP-2M by Tanuma *et al.*³⁶

The EAL is not a material parameter like the IMFP but depends on the defining equation for the particular XPS application.^{29,37,38} For example, there is one defining equation for an EAL in terms of the near-exponential decrease of substrate-photoelectron intensity with increasing thickness of an overlayer film on a planar substrate. Another EAL can be defined in terms of the ratio of substrate and overlayer photoelectron intensities and the corresponding intensities for thick films. The EALs for these two applications are not necessarily the same. For example, systematic differences have been found between EALs for thin films of silicon oxynitride and hafnium oxynitride on silicon obtained from different defining equations.³⁸

Like Shard,⁷ we utilized EALs describing the near-exponential attenuation of photoelectrons from a planar substrate with thickness of an overlayer film. For this application, EALs can be conveniently obtained from a NIST database³⁹ or from empirical equations.^{40–43} We

chose here to determine EALs for use in eqs. (1h) and (1i) from the predictive EAL equation of Jablonski and Powell.⁴¹

$$L = \lambda(1 - 0.735\omega), \quad (2)$$

where λ is the IMFP for the substrate photoelectrons in the overlayer film, ω is the single-scattering albedo which is given by

$$\omega = \lambda/(\lambda + \lambda_{tr}), \quad (3)$$

and λ_{tr} is the transport mean free path (TMFP). The TMFP is related to the transport cross section of an elemental solid, σ_{tr} , by $\lambda_{tr} = 1/N\sigma_{tr}$ where N is the density of atoms in the solid. Values of transport cross sections are available from the NIST Electron Elastic-Scattering Cross-Section database⁴⁴ or from an analytical formula⁴⁵ and TMFPs are available from the NIST SESSA database.²⁶ For an alloy or compound, TMFPs can be determined from transport cross sections for the constituent elements weighted by their atomic fractions.²⁹ Equation (2) is expected to be valid for photoelectron emission angles less than 50° with respect to the surface normal.⁴¹

Table 1 shows values of the IMFPs, TMFPs, single-scattering albedos, and EALs for the photoelectron lines and core-shell materials used in our analysis.

RESULTS AND DISCUSSION

Evaluation of the Shard equation

Figures 1 to 4 show ratios of shell thicknesses, T_{NP} , calculated from eq. (1), to the actual shell thicknesses, T , selected for the SESSA simulations as a function of T for the Au-core/C-shell, C-core/Au-shell, Cu-core/Al-shell, and Al-core/Cu-shell NPs, respectively. Each Figure has separate plots of T_{NP}/T for the chosen core diameters, D , of 1 nm, 2 nm, 5 nm, 10 nm, 20 nm, 50 nm, 100 nm, and 200 nm. Separate simulations were made for each core-shell material combination to determine the photoelectron intensities for the relevant materials (i.e., the C 1s, Au 4f_{7/2}, Al 2p_{3/2}, and Cu 2p_{3/2} signals, as appropriate for the chosen core and shell materials) and for shell thicknesses between 0.25 nm and 3 nm in increments of 0.25 nm. There were thus 96 combinations of core diameter and shell thickness for each core-shell material combination. Values of A were computed with eq. (1g) from the peak intensities I_1 and I_2 for the shell and core materials, respectively, and from corresponding values of I_1^∞ and I_2^∞ obtained from separate simulations for planar samples.

Figure 1 for Au-core/C-shell NPs shows values of T_{NP}/T that are larger than unity. These values were larger than 1.1 only for three NPs with an Au-core diameter of 1 nm and C-shell thicknesses of 0.25 nm, 0.5 nm, and 0.75 nm and for three NPs with Au diameters of 50 nm,

100 nm, and 200 nm and a C-shell thickness of 0.25 nm. The average value of T_{NP}/T for the results in Figure 1 was 1.06.

Figure 2 for the C-core/Au-shell NPs shows values of T_{NP}/T that are mostly less than unity. These values were less than 0.9 for 13 of the 96 core-shell combinations and occurred for an Au-shell thickness of 0.25 nm and C-core diameters between 5 nm and 200 nm and for some Au-shell thicknesses between 0.5 nm and 1 nm and C-core diameters of 5 nm, 10 nm, and 20 nm. The average value of T_{NP}/T for the results in Figure 2 was 0.95.

The plots of T_{NP}/T in Figures 3 and 4 for Al-core/Cu-shell and Cu-core/Al shell NPs, respectively, show more structure as a function of shell thickness than those in Figures 1 and 2. They also have values of T_{NP}/T that are both larger and smaller than unity. For the Al-core/Cu-shell NPs in Figure 3, there is only one NP (Al-core diameter of 2 nm and Cu-shell thickness of 0.5 nm) for which T_{NP}/T was larger than 1.1. The average value of T_{NP}/T for the results in Figure 3 was 1.00.

For the Cu-core/Al-shell NPs in Figure 4, there were six NPs with values of T_{NP}/T less than 0.9. Five of these were for an Al-shell thickness of 0.25 nm and Cu-core diameters between 10 nm and 200 nm and the other was for a Cu-core diameter of 5 nm and an Al-shell thickness of 1.25 nm. The average value of T_{NP}/T for the results in Figure 4 was 0.97.

Of the 768 values of T_{NP}/T shown in Figures 1 to 4, the average value was 1.00 and all but 26 were within 10 % of unity. We consider this result to be a satisfactory validation of the Shard equation for determining shell thicknesses of core-shell NPs by XPS since the uncertainties of the IMFPs from which EALs were derived have estimated uncertainties of $\approx 10\%$.²⁹ We also point out that our evaluation was based on four core-shell material combinations for which the values of B [eq. (1h)] and C [eq. (1i)] in the Shard equation varied between 0.46 and 2.21 and between 0.39 and 2.56, respectively. That is, we have considered material combinations that are expected from Shard's analysis⁸ to yield larger uncertainties in derived shell thicknesses.

Effects of Elastic Scattering on Photoelectron Intensities

We performed a second set of SESSA simulations that were identical to those described above except for elastic scattering being switched off. We then determined values of the parameter A in the Shard equation [eq. (1g)] that we designate as A_{ne} for values obtained when elastic scattering was turned off. We will now compare these values with the corresponding values of A that we obtained previously with elastic scattering switched on and which we now designate as A_{e} .

Figure 5 shows plots of A_{e} and A_{ne} for Au-core/C-shell NPs as a function of core diameter, and similar plots are shown in the Supplementary Information for C-core/Au-shell, Al-core/Cu-shell, and Cu-core/Al-shell NPs. The plots are shown for selected shell thicknesses between 0.5 nm and 3 nm. The plotted values of A_{e} range between 0.37 and 265.6 for Au-core/C-shell NPs, between 0.86 and 2743 for C-core/Au-shell NPs, between 1.04 and 1230 for Al-core/Cu-shell NPs, and between 0.54 and 941 for Cu-core/Al-shell NPs. The corresponding values of A_{ne} range between 0.33 and 291.8, between 0.68 and 1635, between

0.86 and 986.2, and between 0.46 and 703.9 for Au-core/C-shell, C-core/Au-shell, Al-core/Cu-shell, and Cu-core/Al-shell NPs, respectively. That is, the A values in Figure 5 and Figures S1, S2, and S3 can change by approximately three orders of magnitude for the chosen range of core diameters and shell thicknesses.

Our plots of A_{ne} for Au-core/C-shell NPs in Figure 5(b) are qualitatively similar to results obtained by Torelli *et al.*¹³ who investigated Au NPs of different diameters that were functionalized with HS-(CH₂)₁₁-(EG)₆-OH ligands (where EG refers to the ethylene glycol group, -OCH₂CH₂-). They determined shell thicknesses from a computational model in which elastic-scattering effects were neglected.

It is instructive now to examine plots of $R = A_e/A_{\text{ne}}$ versus core diameter in Figure 6 for (a) Au-core/C-shell NPs, (b) C-core/Au-shell NPs, (c) Al-core/Cu-shell NPs, and (d) Cu-core/Al-shell NPs for shell thicknesses between 0.5 nm and 3 nm. We see that R increases approximately linearly with core diameter for core diameters between 1 nm and 20 nm and then is roughly constant for core diameters between 20 nm and 200 nm. There are only small changes in R with shell thickness for Au-core/C-shell NPs in Figure 6(a), larger changes for Al-core/Cu-shell and Cu-core/Al-shell NPs in Figures 6(c) and 6(d), respectively, and much larger changes for C-core/Au-shell NPs in Figure 6(b).

We can semi-quantitatively interpret the major trends in Figure 6 in terms of the single-scattering albedo, ω , from eq. (3) for the *shell* material. For Au-core/C-shell NPs, the values of R are between 0.91 and 0.95 for an Au-core diameter of 1 nm and between 1.09 and 1.11 for an Au-core diameter of 200 nm. That is, the maximum effects of elastic scattering are generally less than about 10 %. These relatively small values of R and of the changes in R with Au-core diameter and C-shell thickness in Figure 6(a), compared to those in Figures 6(b), 6(c), and 6(d), are due to the relatively small values of ω for C 1s and Au 4f_{7/2} photoelectrons in C, 0.073 and 0.064 (Table 1), respectively. The results in Fig. 6(a) also indicate that the neglect of elastic-scattering effects by Torelli *et al.*¹³ in their determination of ligand densities of organic shells on Au-core NPs is reasonable.

The values of R in Figure 6(b) for C-core/Au-shell NPs are much larger than those in Figure 6(a) for Au-core/C-shell NPs, and there are also larger variations with shell thickness. For a C-core diameter of 1 nm, the values of R in Figure 6(b) range between 1.12 and 1.68 while the values of R are between 1.27 and 2.18 for a C-core diameter of 200 nm. The effects of elastic scattering are clearly much stronger than for Au-core/C-shell NPs. We also see that the values of ω for C 1s and Au 4f_{7/2} photoelectrons in Au, 0.352 and 0.346 (Table 1), respectively, are relatively large. We note here that for XPS with Al or Mg K α X-rays and photoelectron kinetic energies between 200 eV and 1.45 keV, ω can vary between about 0.05 (weak elastic-scattering effects) and about 0.45 (strong elastic-scattering effects).^{29,37}

The values of R in Figure 6(c) for Al-core/Cu-shell NPs and in Figure 6(d) for Cu-core/Al-shell NPs are intermediate between those in Figures 6(a) and 6(b). For an Al-core diameter of 1 nm, the values of R are between 1.08 and 1.25 while the R values are between 1.20 and 1.51 for an Al-core diameter of 200 nm. For a Cu-core diameter of 1 nm, R is between 0.98 and 1.34 while the R values are between 1.16 and 1.61 for a Cu-core diameter of 200 nm.

The values of ω are 0.277 and 0.387 for Al 2p_{3/2} and Cu 2p_{3/2} photoelectrons, respectively, in Cu while the values of ω are 0.108 and 0.189 for Al 2p_{3/2} and Cu 2p_{3/2} photoelectrons, respectively, in Al.

Further insights into the variations of R shown in Figure 6 can be obtained from the similar plots shown in Figure 7 for (a) C-core/C-shell NPs, (b) Al-core/Al-shell NPs, (c) Cu-core/Cu-shell NPs, and (d) Au-core/Au-shell NPs. With SESSA, it is possible to obtain separate peak intensities for a given element that is present in both the core and the shell of a NP. As in our previous work for Cu-core/Cu-shell NPs,¹⁶ we placed a tag on a selected photoelectron peak from the core material (say) to distinguish it from the corresponding intensity for the shell material.

Figure 7(a) shows plots of R for C 1s photoelectron intensities from C-core/C-shell NPs as a function of the C-core diameter for the indicated C-shell thicknesses. The values of R gradually increase from near unity for a C-core diameter of 0.5 nm to an average value of about 1.06 for a C-core diameter of 200 nm. For each value of the C-core diameter, the values of R vary by between about 3 % and 5 %.

Similar trends are seen in Figures 7(b), (c), and (d) for Al-core/Al-shell, Cu-core/Cu-shell, and Au-core/Au-shell NPs, respectively, but the variations of R with core diameter and shell thickness are larger than in Figure 7(a). While the changes in R for Al-core/Al-shell NPs in Figure 7(b) are slightly larger than those in Figure 7(a), the changes in R for Cu-core/Cu-shell NPs in Figure 7(c) and for Au-core/Au-shell NPs in Figure 7(d) are much larger than those in Figure 7(a). For example, the average value of R in Figure 7(c) changes from 1.63 for a Cu-core diameter of 1 nm to an average value of 2.26 for a Cu-core diameter of 200 nm. In addition, R changes from 1.10 to 2.38 for Cu shell thicknesses of 0.5 nm and 3 nm, respectively, and a Cu-core diameter of 1 nm, while R changes from 1.42 to 3.37 for Cu-shell thicknesses of 0.5 nm and 3 nm, respectively, for a Cu-core diameter of 200 nm.

The changes of R with core diameter and shell thickness in Figure 7 roughly correlate with values of the single-scattering albedo for the relevant photoelectron lines in Table 1. The values of ω are 0.073 for C 1s photoelectrons in C, 0.108 for Al 2p_{3/2} photoelectrons in Al, 0.387 for Cu 2p_{3/2} photoelectrons in Cu, and 0.346 for Au 4f_{7/2} photoelectrons in Au. That is, the elastic-scattering effects are expected to be relatively weak for C 1s photoelectrons in C and for Al 2p_{3/2} photoelectrons in Al, and to be much stronger for Cu 2p_{3/2} photoelectrons in Cu and for Au 4f_{7/2} photoelectrons in Au, as seen in Figure 7. There are also second-order effects associated with the dimensions of the core and shell for all materials studied.

Comparisons with other Techniques

The determination of shell thicknesses of NPs is extremely important for many applications, and a combination of techniques is often needed.^{9,24} For example, it is difficult to obtain statistically significant results with transmission electron microscopy (TEM), and therefore the combination of TEM and XPS is very powerful. For example, TEM enables an assessment of heterogeneity in a group of NPs while XPS can provide a statistically valid mean value. In a recent study, Wang *et al.*¹⁶ showed that a combination of TEM, XPS, and simulations with SESSA enabled more complete characterizations of Au-core/Ag-shell NPs

after various surface treatments. In another application, Rafati *et al.*²¹ employed TEM, XPS, time-of-flight secondary-ion mass spectrometry, attenuated-total-reflectance Fourier infrared spectroscopy, and low-energy ion scattering (LEIS) to characterize oligo(ethylene glycol) functionalized gold NPs. We also note that Belsey *et al.*⁴⁶ used ultraviolet-visible spectroscopy, dynamic light scattering and differential centrifugal sedimentation of NPs in a liquid suspension as well as XPS of dried samples to quantify protein films adsorbed on Au NPs. Finally, we point out that Sublemontier *et al.*⁴⁷ measured shell thicknesses of Si-core/SiO₂-shell NPs by XPS and TEM. These authors concluded that the XPS measurements were more accurate than the TEM measurements.

While TEM is a powerful technique for the characterization of NPs, we point out that dimensional measurements depend on the observation of sufficient contrast between two adjacent phases. Further, defining an interface position can be challenging, as evidenced by the average 0.80 nm offset in TEM measurements of the thicknesses of SiO₂ films on planar Si substrates in comparisons with measurements by other methods.⁴⁸ TEM measurements of shell thicknesses of core-shell NPs are likely to be more challenging, particularly for shells comprised of organic materials or for NPs with core and shell materials of similar atomic numbers where lack of contrast is an issue. Even for Au-core/Ag-shell NPs, advanced scanning-TEM instrumentation was needed to obtain useful images.¹⁶

An interlaboratory comparison has been made of measurements of peptide thicknesses on functionalized Au NPs by XPS and LEIS.⁴⁹ Different algorithms were used by the XPS participants, and there was a variability of 67 % in the reported shell thicknesses. However, a variability of only 12 % was obtained among the participants who used the Shard equation and who chose photoelectron peaks that were not adversely affected by instrumental transmission effects. The results from the LEIS participants were more consistent.

SUMMARY

We evaluated two approaches for determining shell thicknesses of core-shell NPs by XPS. Our evaluations were based on simulations of photoelectron peak intensities using the NIST SESSA database. These simulations were performed for Au-core/C-shell NPs, C-core/Au-shell NPs, Cu-core/Al-shell NPs, and Al-core/Cu-shell NPs with core diameters of 1 nm, 2 nm, 5 nm, 10 nm, 20 nm, 50 nm, 100 nm, and 200 nm, and with shell thicknesses between 0.5 nm and 3 nm in increments of 0.5 nm. We determined intensities of the C 1s, Al 2p_{3/2}, Cu 2p_{3/2}, and Au 4f_{7/2} photoelectron peaks, as appropriate for the core and shell materials, that were excited by Al K α X-rays.

We previously evaluated use of the Shard equation⁸ for determining shell thicknesses using simulated Cu 2p_{3/2} intensities from Cu-core/Cu-shell NPs with a wide range of core diameters and shell thicknesses.¹⁷ This work was extended here with core-shell material combinations that have suitably large or small combination values of the parameters *B* and *C* in the Shard equation for our selected photoelectron signals. We determined values of shell thicknesses, *T*_{NP}, from the Shard equation from the SESSA simulations for each core-shell material combination and for the selected core and shell dimensions. These values were compared with the actual shell thicknesses, *T*, chosen for each simulation. Of the 768 values

of T_{NP}/T , the average value was 1.00 and all but 26 were within 10 % of unity. We consider this result to be a satisfactory validation of the Shard equation since the uncertainties of inelastic mean free paths (the key material parameter on which effective attenuation lengths depend) have estimated uncertainties of about 10 %.²⁹ We also note that the values of the parameters B and C varied between 0.46 and 2.21 and between 0.39 and 2.56, respectively. These ranges for B and C are expected from Shard's analysis to yield larger uncertainties in derived shell thicknesses than if B and C were each closer to unity.

We also examined ratios of photoelectron peak intensities from the shell and core materials (the A parameter in the Shard equation) for the Au-core/C-shell NPs, C-core/Au-shell NPs, Al-core/Cu-shell NPs, and Cu-core/Al shell NPs. Values of A were determined from our SESSA simulations with elastic scattering switched on in SESSA, A_{e} , and compared with values of A that were determined from similar simulations with elastic scattering switched off, A_{ne} . Our values of A_{ne} for Au-core/C-shell NPs were qualitatively similar to those of Torelli *et al.*¹³ who determined peak intensities from a model in which elastic-scattering effects were neglected. We plotted values of the ratio $R = A_{\text{e}}/A_{\text{ne}}$ as a function of core diameter and shell thickness to show the magnitudes of elastic-scattering effects on the photoelectron intensities. These plots showed that these effects were generally less than about 10 % for Au-core/C-shell NPs, an important result that justifies the neglect of elastic scattering in analytical models that are applied to organic ligands on Au-core NPs.¹³ Nevertheless, R could vary between 1.12 and 2.18 for C-core/Au-shell NPs, with specific values depending on the core diameter and the shell thickness; that is, elastic-scattering effects on the ratios of peak intensities varied between about 10 % and 120 %. Values of R for Al-core/Cu-shell and Cu-core/Al-shell NPs varied between 0.98 and 1.61, and again depended in detail on the core diameter and shell thickness.

We also determined values of R for C-core/C-shell NPs, Al-core/Al-shell NPs, Cu-core/Cu-shell NPs, and Au-core/Au-shell NPs for the same range of core diameters and shell thicknesses as before. These results indicated that there was a rough correlation between R and values of the single-scattering albedo for each material and that there were second-order dependences on core diameter and shell thickness. In general, elastic-scattering effects are relatively small (less than about 15 %) for C-core/C-shell and Al-core/Al-shell NPs but can be much larger (between 10 % and a factor of about 3.4) for Cu-core/Cu-shell and Au-core/Au-shell NPs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Plots of the ratio of values of the shell thickness T_{NP} from eq. (1) to the actual shell thickness, T , as a function of T for Au-core/C-shell NPs from SESSA simulations as described in the text, (a) Au-core diameters, D , of 1 nm, 2 nm, 5 nm, and 10 nm; (b) Au-core diameters, D , of 20 nm, 50 nm, 100 nm, and 200 nm.

Figure 2.
As for Figure 1 except for C-core/Au-shell NPs.

Figure 3.
As for Figure 1 except for Al-core/Cu-shell NPs.

Figure 4.
As for Figure 1 except for Cu-core/Al-shell NPs.

Figure 5.

Plots of (a) A_e , the value of the parameter A in the Shard equation [eq. (1g)] when elastic scattering was switched on in the SESSA simulations, and (b) A_{ne} , the value of the parameter A in the Shard equation [eq. (1g)] when elastic scattering was switched off in the SESSA simulations, for Au-core/C-shell NPs as a function of core diameter and for selected shell thicknesses between 0.5 nm and 3 nm.

Figure 6.

Plots of $R = A_e/A_{ne}$ versus core diameter for (a) Au-core/C-shell NPs, (b) C-core/Au-shell NPs, (c) Al-core/Cu-shell NPs, and (d) Cu-core/Al-shell NPs and the indicated shell thicknesses. These plots were made with C 1s, Al 2p_{3/2}, Cu 2p_{3/2}, and Au 4f_{7/2} peak intensities from SESSA simulations with (for A_e) and without (for A_{ne}) inclusion of elastic scattering. Note the changes in the ordinate scales for the different panels.

Figure 7.

Plots of $R = A_e/A_{ne}$ versus core diameter for (a) C-core/C-shell NPs, (b) Al-core/Al-shell NPs, (c) Cu-core/Cu-shell NPs, and (d) Au-core/Au-shell NPs and the indicated shell thicknesses. These plots were made with C 1s, Al 2p_{3/2}, Cu 2p_{3/2}, and Au 4f_{7/2} peak intensities from SESSA simulations with (for A_e) and without (for A_{ne}) inclusion of elastic scattering. Note the changes in the ordinate scales for the different panels.

Table 1

Values of photoelectron energies, inelastic mean free paths (IMFPs), transport mean free paths (TMFPs), single-scattering albedos (ω), and effective attenuation lengths (EALs) used for the photoelectron lines in the designated materials that were used in the SESSA simulations and in the analysis of the results.

Photoelectron Line	Material	Kinetic Energy (eV)	IMFP (nm)	TMFP (nm)	ω	EAL (nm)
Au 4f _{7/2}	Au	1403	1.73	3.27	0.346	1.29
Au 4f _{5/2}	C	1403	3.48	50.84	0.064	3.32
C 1s	Au	1202	1.54	2.84	0.352	1.14
C 1s	C	1202	3.08	38.97	0.073	2.91
Al 2p _{3/2}	Al	1414	2.83	3.35	0.108	2.61
Al 2p _{1/2}	Cu	1414	2.19	5.73	0.277	1.75
Cu 2p _{3/2}	Al	554	1.37	5.86	0.189	1.18
Cu 2p _{1/2}	Cu	554	1.12	1.78	0.387	0.80