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Low energy ion scattering: Determining overlayer thickness for functionalized gold nanoparticles

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Abstract

With the widespread use of engineered nanoparticles for biomedical applications, detailed surface characterization is essential for ensuring reproducibility and the quality/suitability of the surface chemistry to the task at hand. One important surface property to be quantified is the overlayer thickness of self-assembled monolayer (SAM) functionalized nanoparticles, as this information provides insight into SAM ordering and assembly. We demonstrate the application of high sensitivity low energy ion scattering (HS-LEIS) as a new analytical method for the fast thickness characterization of SAM functionalized gold nanoparticles (AuNPs). HS-LEIS demonstrates that a complete SAM is formed on 16-mercaptohexadecanoic acid (C16COOH) functionalized 14 nm AuNPs. HS-LEIS also experimentally provides SAM thickness values that are in good agreement with previously reported results from simulated electron spectra for surface analysis (SESSA) analysis of X-ray photoelectron spectroscopy (XPS) data. These results indicate HS-LEIS is a valuable surface analytical method for the characterization of SAM functionalized nanomaterials.

Keywords

Gold nanoparticles; SESSA; HS-LEIS; overlayer thickness; characterization; XPS

Introduction

In recent years there has been an increased research interest in colloidal AuNPs, with new production protocols that utilize alkanethiol self-assembled monolayers (SAMs) to stabilize and provide a range of surface properties for the AuNPs.¹⁻³ Many groups that use biomedical AuNPs emphasize the properties resulting from the high surface to bulk atomic ratio of AuNPs, such as reactivity and unique optical properties, but neglect detailed surface characterization⁴. The surface analysis of SAM functionalized nanomaterials is a significant challenge due to the surface curvature and faceting present in nanoparticles. However quantitative surface characterization of these materials is essential to ensure the quality of the surface chemistry, coverage and reproducibility.⁵⁻¹³ The use of the SESSA software¹⁴ to model XPS data for SAM functionalized AuNPs has previously been achieved by using data from a flat sample acquired at nine different take-off angles to determine the thickness and composition of the SAM layer.¹⁵ For a C16COOH SAM, SESSA showed the SAM was 14 % thinner on the surface of a 14 nm AuNP (1.85 nm) than on a flat substrate (2.15 nm). This observation indicates either a more tilted thiol molecules or a greater level of disorder in the

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SAM on the AuNPs. Such knowledge allows for an improved understanding of AuNPs results in biomedical applications.

In traditional LEIS analysis a sample is exposed to low energy noble gas ions and the scattering of these incident ions and subsequent energy loss of the detected scattered ions can be directly related to the elemental composition of the outermost surface. Recent advances in HS-LEIS instrumentation provides greater sensitivity for analysis of different atomic layers along with a significant reduction in surface damage, now allowing the technique's static depth profiling capability to be applied to NP characterization.^{16,17} The reduced sample damage achieved in new HS-LEIS instrumentation allows for accurate thickness measurements of organic thin films. Previously beam damage would accumulate over the course of the sample analysis, resulting in degradation of the film and compromising the measurements. We report here the results from using the HS-LEIS method to determine the overlayer thickness for SAM functionalized AuNPs.

Experimental

Materials and reagents

Hydrogen tetrachloroaurate (III) trihydrate (99.9% $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium citrate dihydrate (trisodium salt, $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), 16-mercaptohexadecanoic acid (C_{16}COOH) were purchased from Sigma-Aldrich. Ethanol (absolute-200 proof) was purchased from Pharmaco-AAPER (Vancouver, WA). Ultrapure water (resistivity $> 18.2\text{ MG}/\text{cm}$) dispensed by a Modulab Analytical research-grade water system (Siemens, Lowell, MA) was used in all sample preparation and for all glassware cleaning. All reagents were used as received and were of analytical grade.

Dialysis tubing (Spectra/Por, regenerated cellulose, MWCO 50,000) was purchased from VWR Scientific Inc. TEM grids (Carbon Type-A, 300 mesh, copper grids) were purchased from Ted Pella Inc. (Redding, CA). Silicon wafers were purchased from Silicon Valley Microelectronics and diced into $1\text{ cm} \times 1\text{ cm}^2$ pieces and then cleaned with a series of organic solvent washes. Flat gold substrates were produced by coating the Si wafer pieces at pressures below 1×10^{-6} torr with a 10 nm film of titanium followed by 100 nm of gold (99.9%) using a CHA 600 Electron Beam Evaporator.

AuNP synthesis and functionalization

Gold nanoparticles were synthesized using the Frens modified Turkevich method described elsewhere.^{18–20} Briefly, glassware was cleaned with aqua regia (HCl/HNO_3 in a 3:1 ratio) to remove any previous gold contamination and rinsed with copious amounts of ultrapure water to remove any acid residue. A 0.01% (w/v) HAuCl_4 aqueous solution was heated to 100°C and maintained at this temperature for the entire synthesis in a reflux system under nitrogen. A 1% aqueous solution of $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ was added in a volumetric ratio of 2.5:100 to make particles with an average diameter of 14 nm. The synthesis was allowed to continue for 30 mins then allowed to cool to room temperature before being stored at 4°C until required for analysis.

A 1mM stock ethanol solution of the thiol was first prepared. A $2\times$ excess concentration of $100\text{ }\mu\text{M}$ of C_{16}COOH was added to 100 mL of AuNPs and sonicated for 1 min after 2 mins of stirring, then left to functionalize for 2 days under stirring on a magnetic stirrer plate. An Allegra X-22 series centrifuge (Beckman Coulter, California, USA) was used to spin the 14 nm functionalized AuNPs at 8,000 RPM for 45 mins. The supernatant was extracted and discarded. Dialysis was then done to remove any unbound thiol and other impurities using at least 15 water changes.²⁰ The concentrated AuNPs were deposited $10\text{ }\mu\text{L}$ at a time on the solvent cleaned silicon pieces and placed under vacuum in a desiccator to form a sufficiently

thick film of AuNPs for XPS and HS-LEIS analysis. A complete layer was desirable to avoid any background signal from the underlying silicon substrate.

Characterization Methods

A Phillips CM100 transmission electron microscope operating at 100 kV accelerating voltage was used to image the AuNPs. Images were acquired with a Gatan model 689 digital slow scan camera (Gatan Inc., Pleasanton, CA). All images had 128×128 pixels at either 130k or 180k magnification. The images were processed using ImageJ (ver. 1.46, NIH, Maryland, USA) to determine the average size and circularity of the synthesized AuNPs before functionalization.

A Kratos Axis Ultra DLD (Kratos, Manchester, UK) equipped with a monochromatic Al K X-ray source operated at 150 watts was used for all XPS data acquisition. Samples were analyzed in duplicate with at least 3 spots per sample. Detailed spectra were acquired at an analyzer pass energy of 80 with step sizes of 1 eV for the survey spectra and 0.3 eV for detailed spectra using a dwell time of 250 ms. High resolution spectra were acquired at a pass energy of 20 with a step size of 0.1 eV for all spectral regions and the dwell time for the S2p, C1s and Au4f spectral regions were 425.5, 259.7 and 458.0 ms, respectively. XPS determined elemental compositions were calculated using manufacturer provided sensitivity factors and linear backgrounds. CasaXPS (ver. 2.3.16) was used for all XPS data analysis.

HS-LEIS analysis was performed with an ION-TOF Qtac¹⁰⁰ (IONTOF GmbH, Münster, Germany) dedicated HS-LEIS instrument using a scattering angle of 145 degrees. The analysis of the samples was performed using 5 nA, 3 keV $^4\text{He}^+$ primary ions scanned over an area of $2 \times 2 \text{ mm}^2$. The analysis took 180 s, leading to an ion dose of 1.4×10^{14} ions/cm², which is well below the static limit for 3 keV He ions. A flat gold reference sample was analyzed after sputter cleaning with 500 eV Ar⁺. For the flat gold reference sample the sputter beam was scanned over $1.5 \times 1.5 \text{ mm}^2$ while the analysis beam was scanned over $0.75 \times 0.75 \text{ mm}^2$.

A Bruker Tensor 27 was used for ATR-FTIR analysis. $1 \times 1 \text{ cm}^2$ flat pieces of Au coated Si, either with or without 1H,1H,2H,2H, perfluorododecane-1-thiol (Assemblon, WA, USA) overlayers were used as background references. Similar spectra and stretching frequencies were observed using both background references. Data was collected in 2 cm^{-1} steps and summed over 80 scans.

Results and Discussion

Particle sizing and comparison to literature data

TEM analysis was used to determine the size and shape distribution of the synthesized AuNPs, as shown in Figure 1. The 14 nm AuNPs have a narrow normal distribution, as determined from sampling ~4,400 AuNPs with the particle analysis functionality of the ImageJ analysis software. On average the particles were found to exhibit circularity with 81% of the particles analyzed observed to have a height to width ratio lower than 1.1, which for this study is considered spherical. Those particles that appeared non-spherical were more triangular in shape, likely due to a high expression of larger 111 terraces. These particles however make up a minority of particles samples but this is a source of error for analysis protocols which assume a spherical particle.¹⁵

SESSA¹⁴ is a simulation program capable of modeling XPS data from flat surfaces, but has recently been shown to be able to provide good agreement for 14nm AuNPs functionalized with C16COOH SAMs.¹⁵ Briefly, in that study the C16COOH SAM was modeled in SESSA as 18 layers (individual methylene groups with a 0.9 Å space between groups, a

thiol anchor group and a carboxyl termination) for 9 photoelectron take-off angles from 5° to 85°. A geometric correction was applied to the data to model a spherical nanoparticle surface as 9 concentric cylinders. Also, from comparison of the SESSA to the experimental results it was shown a 1.5 Å hydrocarbon contamination layer was present on the surface of these samples.¹⁵ With HS-LEIS analysis a more direct method of the total organic overlayer thickness (SAM plus any contamination layer) measurement is possible. The data in this work is acquired over a 2 mm² analysis area to provide experimental results for comparison with the SESSA simulations. The XPS determined elemental compositions for the new samples prepared for the HS-LEIS experiments were consistent with those reported by Techane *et al*¹⁵ (69.4±0.6 atomic % carbon, 9.7±0.4 atomic % oxygen, 1.5±0.2 atomic % sulfur and 19.4±0.8 atomic % gold). Thus, we consider SESSA results from the study of Techane *et al* applicable to the analysis presented in this paper.

Examples of XPS data acquired from the SAM covered AuNPs are shown in Figure 2. The survey spectrum shows the expected peaks from gold, carbon, oxygen and sulfur. The high resolution C1s spectrum is dominated by the hydrocarbon peak at 285 eV from the 16 methylene groups in each thiol molecule with a small peak near 289 eV from the carboxylic acid terminal group of the thiol. The high resolution S2p spectrum exhibits a doublet from the S2p_{3/2} and S2p_{1/2} peaks of a bound thiol (S2p_{3/2} BE of 162 eV), indicating all the thiol molecules in the SAM are attached to the surface of the AuNPs via a gold-thiolate bond.

HS-LEIS analysis

While HS-LEIS is best known for the ability to give a quantitative element analysis of the outermost atomic layer, it is also capable of giving static (non-destructive) depth profiles over the outermost 5–10 nm of a sample.^{17,21–23} The peaks in the HS-LEIS spectrum are caused by scattering from surface atoms (i.e., the outermost atomic layer). The background is due to scattering by heavier atoms, such as gold, from deeper layers. HS-LEIS is surface sensitive due to the use of noble gas ions. Though these particles scatter from deeper layers as well as the surface, the noble gas ions are neutralized as soon as they penetrate the sample, making them undetectable. However, a very small fraction of the neutrals that are scattered from deeper layers are re-ionized as they leave the sample. This fraction is small enough that it doesn't significantly interfere with the signal from the surface atoms, but large enough to give rise to a background that can be interpreted and used for subsequent determination of overlayer thickness.

This background is observed on the low energy side of the "surface peak" of the element being studied, since the primary particle has lost energy while traveling through the SAM before and after the scattering event. The amount of energy that is lost depends on the path length and hence on the depth of the scattering atom. Therefore, the energy scale in the HS-LEIS spectrum can be converted to a depth scale where the intensity of the background corresponds to the density of the element in the layer. For SAMs on Au it is possible to analyze the Au concentration profile with this method. This will then yield the thickness of the layer by differentiation of the Au depth profile. In SAMs, this distribution is narrow and therefore spans a narrow energy range. This means it is not necessary to correct for the variation of re-ionization probability with energy.

The 3 keV ⁴He⁺ HS-LEIS spectra in Figure 3a have been scaled to the same height to allow for comparison of SAM thickness. The arrow indicates the amount of scattered ion energy loss that is proportional to the layer thickness. To determine the thickness of the SAM, the energy of the reionized He⁺ ions scattered from the SAM/AuNP interface is measured and compared with the scattering from He⁺ ions scattered from a clean Au surface. The spectra were fit to an error function as shown in Figure 3b.

The HS-LEIS data was fit to the error function, $Y(E) = a \times (1 - \text{erf}(E, m, s)) + b$. Where $\text{erf}(E, m, s)$ is the error function of the energy E , the integral of the normal distribution with a mean m and a standard deviation s . The parameters a and b are the (constant) intensities on either side of the step: a for the low-energy side and b for the high-energy side. The fitting is done using the SurfaceLab6 software (IONTOF GmbH, Germany) with values for the fits shown in Table 1. The position of the Au peak is determined by fitting it to a Gaussian function after subtracting the background. The center of this Gaussian is used as the energy reference to determine the energy loss. The increased width of the error function, relative to the gold peak width, can be due to (1) peak broadening caused by the particles travelling through the overlayer (e.g., energy straggling), (2) non-uniformity of the overlayer thickness and (3) geometry effects (e.g., curvature of the NPs). The COOH SAMs are well ordered with a uniform thickness, so energy straggling and/or geometric effects likely are the major contributors to the greater error function width. The geometric effects are discussed in more detail below.

As the error function describes the concentration of Au as a function of depth, by differentiation of this function the SAM layer thickness distribution as a function of energy is attained. The energy scale is then converted to a depth scale by comparing the m to the center of the Au reference peak as denoted with an arrow in Figure 3a. The difference in energy value ($E_{\text{reference peak}} - m$) shows the energy lost while the particle travelled through the sample, which is proportional to the layer thickness. The proportionality constant depends on the primary ion energy and also on the mass of the substrate and nature of the adsorbed layer. The error function is most applicable for flat surfaces, however when analyzing a confluent layer of AuNPs we assume this a suitable model for this work. With 3 keV $^4\text{He}^+$ ions for SAMs on Au this constant has been determined to consistently be 90 eV/nm based on previous studies using alkanethiol SAMs on gold.¹⁷ A HS-LEIS determined SAM thickness value of 1.8 nm for the COOH-SAM/14nm AuNPs is consistently observed across three analysis regions, in excellent agreement with the 1.85 nm thickness modeled by SESSA simulations¹⁵ as well as the 1.74 nm thickness approximated by Shard's new XPS modeling method for spherical particles.²⁵ This is consistent with unpublished observations that the LEIS determined thicknesses rarely deviate more than 5% from the values determined by other methods such as atomic force microscopy, X-ray reflection and sputter depth profiling.

It is important to note that the thickness value determined from the HS-LEIS measurements relies on properly relating the energy loss to an overlayer thickness. Thus, the reference samples used to determine this calibration factor need to match as closely as possible the properties of the samples being analyzed in terms of density, overlayer thickness, etc. For the SAM functionalized AuNPs SAMs on flat gold surfaces were used as a reference. Based on the thickness, ordering, density, etc. for the SAMs being similar on the NP and flat gold surfaces, we assume that the energy loss value obtained from the flat surfaces (90 eV per nm of overlayer thickness) should be appropriate for application to NP surfaces. However, the substrate geometry (flat vs. NP) is significantly different, and geometrical effects need to be considered. The fact that without making any geometrical corrections the HS-LEIS determined thicknesses are the same, within experimental error, as the XPS measurements suggest that the geometric effects are not significant for this HS-LEIS analysis. This is different from XPS, where the geometric effects must be properly accounted for to obtain correct thickness values. A detailed analysis of this difference is beyond the scope of this paper so the geometric effects in HS-LEIS analysis of NPs are not considered in this work, but are assumed to be minor. Also, we note that during HSLEIS the scattering of particles striking the top of the NP at normal incidence the scattering process for the NP is essential the same as for a flat surface. As the incident particle strikes the NP near the top, but slightly to one side, different exit paths now become possible. Some are similar to or possibly

shorter than the flat surface path. Others are longer, traveling through the overlayer and exiting towards the other side of the NP. As the incident particle strikes the NP further away from the top of the NP the longest exit paths become blocked by the gold core, eliminating these contributions to the HS-LEIS signal. Also as the incident particle strikes the NP further away from the top of the NP, the path lengths for the scattering conditions that can reach the detector become longer, but the scattering conditions, relative to the surface of the gold core, become more unlikely for those paths. Thus, there is some level of preference that favors scattering path lengths from the AuNPs that are the most similar to the flat surface. The numerical agreement between the SESSA and LEIS results suggests that the flat film analysis approach applies reasonably well for nanoparticles and that the majority of the detected scattering events originate from the top of the NP where the flat surface and NP path lengths are similar.

The HS-LEIS analysis is able to confirm the SAM layers completely cover the AuNP surface since no Au surface peak at ~2700 eV is detected in the COOH-SAM AuNP spectrum (see Figure 3a). The ATR-FTIR results in Figure 3c indicate a high degree of ordering and crystallinity in the alkanethiol backbone as shown by the CH₂ stretching frequencies.²⁴ When interpreting the thickness measurements it is important to know whether or not the overlayer is well ordered and the orientation of the molecules in the overlayer since both can effect the overlayer thickness. The presence of an ordered SAM is consistent with the HS-LEIS data that shows formation of a complete monolayer on the AuNP surface.

Conclusions

We have shown for the first time that XPS modeling with SESSA, a less detailed XPS analysis using the approach by Shard and HS-LEIS produce SAM thicknesses that are the same within experimental error. All three analysis methods show the C16COOH SAM on the 14 nm AuNPs is ~0.3nm thinner than on a flat substrate. HS-LEIS measures the total overlayer thickness and is sensitive to atomic layers in the top ~10 nm of the surface. XPS modeling with SESSA, however can separate the contributions to the total overlayer thickness from the SAM and from the hydrocarbon contamination. HS-LEIS allows for quick measurements with relatively straightforward analysis and interpretation of the results, whereas SESSA currently requires a significantly more involved and lengthy analysis of overlayer thickness on colloidal particles but can provide additional chemical compositional information. This work has shown the two techniques to be complementary for extending XPS data^{12,15,25} and providing quantification of SAM thickness on AuNPs.

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Figure 1.

a) Characteristic TEM image of 14 nm AuNPs with examples of the more triangular particles highlighted with red arrows. b) NP size distribution with the mean and standard deviation shown.

Figure 2. XPS High resolution spectra representative of a) the S2p and b) C1s regions and c) a survey scan showing a lack of significant contamination within the confluent layer of 14 nm AuNPs.

Figure 3.

a) HS-LEIS spectra with an arrow showing the energy difference measured to determine the SAM thickness (FWHM). b) Representative quality of fit for a AuNP sample. c) Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) data showing the CH₂ stretch region.

Table 1

Fit results for the Au reference surface and COOH SAM on 14 nm AuNPs from the HS-LEIS results shown in Figure 3. The standard deviations for each value are listed in parentheses.

Fit Parameter	SAM on AuNPs (in brackets)	Au Reference (in brackets)
a	2.9 (0.4)	4.8 (0.5)
b	0.00 (0.00)	0.01 (0.02)
m	2518 (5)	2702 (1)
s	123 (2)	31 (1)