Determining the Structure of Silver-Coated Gold Nanoparticles Using Anomalous Small Angle X-ray Scattering (ASAXS)

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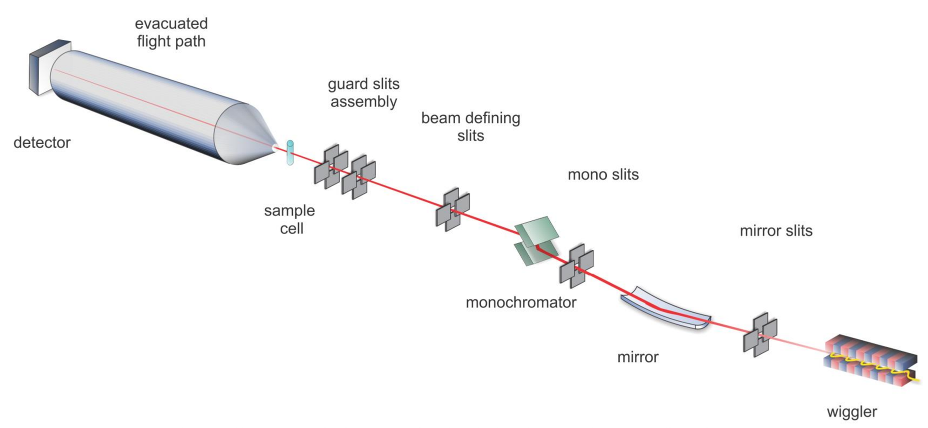
Abstract

An important objective within the field of nanotechnology is to understand how the dispersion of elements within the bimetallic nanoparticles (BNP's) affects the resulting properties. Emerging properties from BNPs represent a field of biomedical and chemical engineering with revolutionary nanobiological solutions. BNPs have been prepared and utilized as antimicrobial agents in wastewater treatment, medical devices, medicinal tolerance solutions, and catalysis. The properties and efficiency of these nanoparticles for various applications depend upon how the two metals are distributed within the nanoparticles. In order to understand the structure-property relationship of these bimetallic nanoparticles, it is important to characterize the distribution of the metals within the core-shell structure. TEM is a common method used to determine information from nanoparticles yet there are issues with this process of collecting data. The most significant issue that arises is that core-shell information is difficult to process since the data is not statistically significant as TEM focuses on information solely from select particles. Techniques like TEM, SEM, and AFM are generally used for characterizing nanomaterials, but they don't provide statistical information about the core shell structure. ASAXS is element-sensitive while also having the ability to produce structural information.

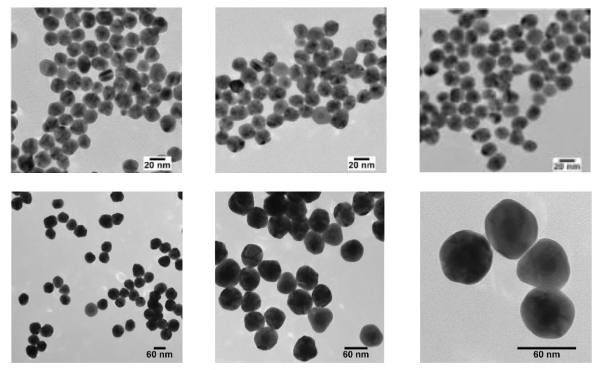
Background

The APS is crucial to this experiment as it provides the necessary flux to observe and accurately detect minute spatial properties of BNPs on a molecular scale. We chose the NSF's ChemMatCARS, Sector 15 of Advanced Photon Source, for this experiment because this beamline has developed optimized instrumentation and analysis tools for accurate ASAXS measurements, components crucial for the success of the proposed experiment.
The two sizes of silver-coated gold nanoparticles tested at the beamline remotely by our cooperating scientists were 20 nanometers and 60 nanometers.



Courtesy: https://www-ssrl.slac.stanford.edu/smb-saxs/content/hardware

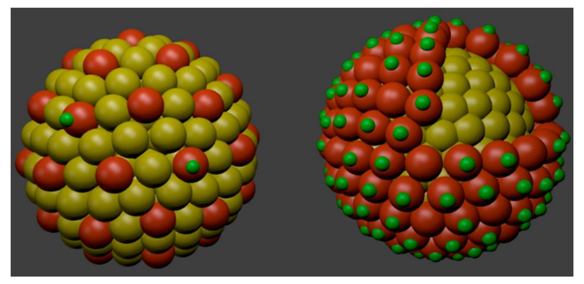
Sample Preparation Procedure



In order to characterize the nanoparticles, our team prepared 4 sets of samples in 1.5 mm quartz capillary tubes in order to obtain ASXAS data and backgrounds. Our samples included an empty capillary tube, a capillary tube filled with H_2O for background subtraction, and two capillary tubes with 20nm and 60nm nanoparticles. As a part of anomalous small angle X-ray scattering (ASAXS) data collection, we performed two sets of SAXS measurements at 20 different energies near the Gold (Au) L3 edge in the range (10.9190-11.9190 eV) and the Silver (Ag) K-edge in the range (24.5140-25.5140 eV). The silver-shelled gold nanoparticles were procured from NanoComposix (https://nanocomposix.com/collections/core-shell-silver-shelled-gold).

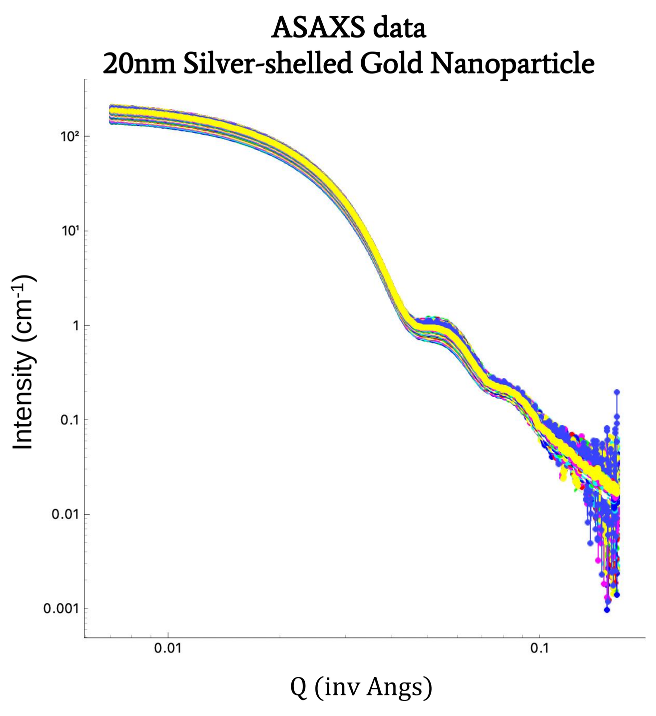
Images courtesy of NanoComposix and Julia Chom

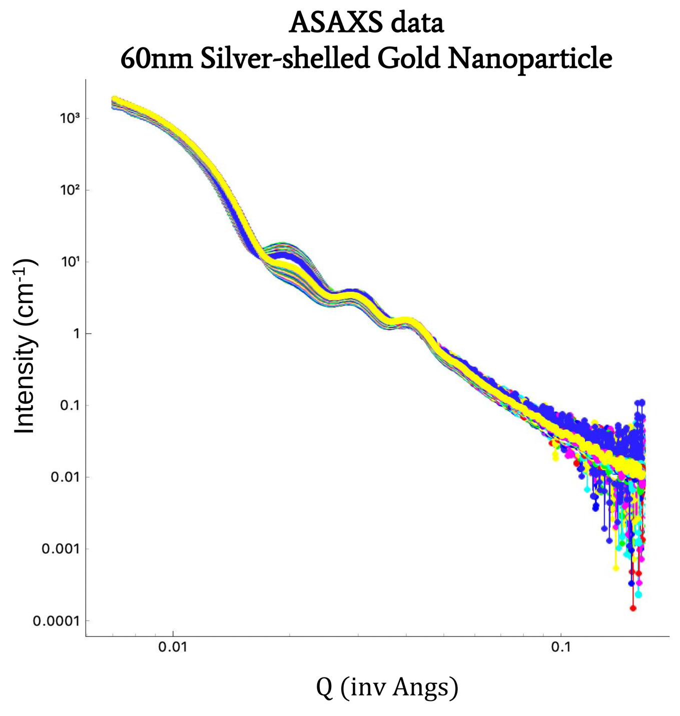
Goals

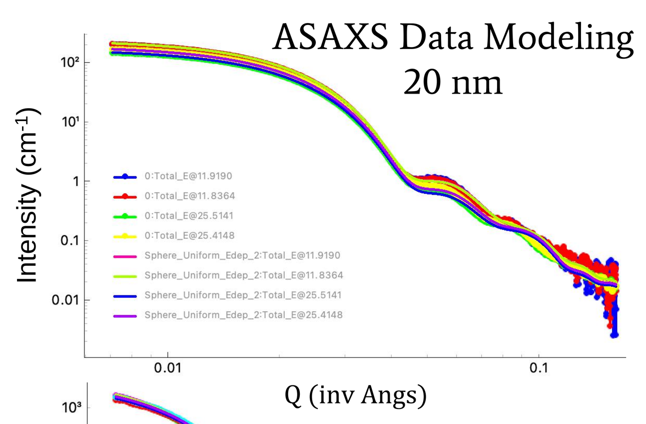


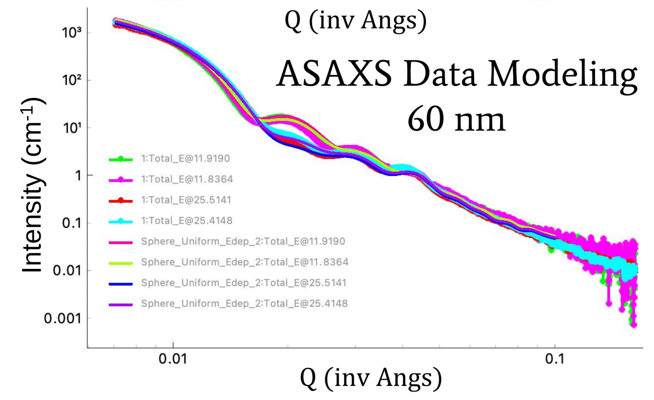
- Determine the relationship between variations of statistical data and how this correlates with the variation of alloys at the macroscopic level.
- Use ASAXS to develop a new, more accurate method of data collection for the analysis of bimetallic nanoparticles.

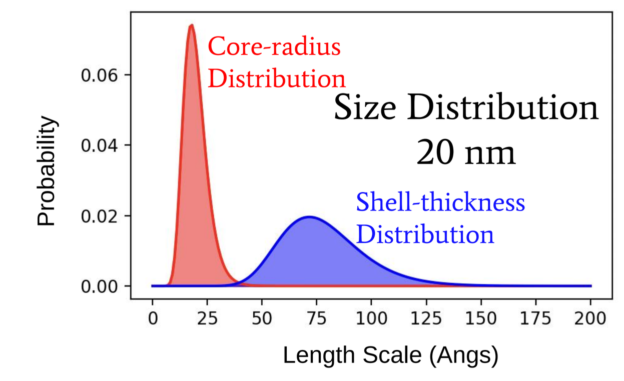
Results











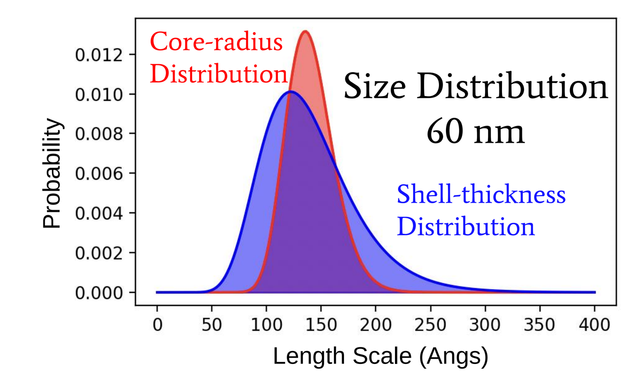


Table 1
Parameters from ASAXS Data Modeling

Particle Size and Sample	Norm (nano-Molar)	Average of Radius Core (Angs)	Average of Shell (Angs)	Average of ΔRadius (Angs)	Average of ΔShell (Angs)	Standard Deviation of Radius Core	Standard Deviation of Shell	Standard Deviation of ΔRadius	Standard Deviation of ΔShell	Average Density of Au (g/cm^3)
20 nm Sample 1	40.4	19.0	75.8	0.28	0.24	0.4	0.3	0.025	0.002	19.32
20 nm Sample 2	40.7	18.4	76.1	0.31	0.24	0.4	0.3	0.028	0.001	19.32
60 nm Sample 1	1.5	138.6	133.6	0.15	0.30	1.0	1.4	0.004	0.003	17.23
60 nm Sample 2	13.6	144.4	132.7	0.16	0.32	2.6	0.5	0.040	0.018	18.04

Table 2
TEM and ASAXS Measurement Comparison

	20 nm (Angs)	60nm (Angs)
TEM-Core-Radius	35	150
TEM-Shell-Thickness	67	150
ASAXS-Core-Radius	19	141
ASAXS-Shell Thickness	76	133

Using TEM and data modeling, elements of the silver-shelled gold nanoparticles can be distinguished and a general value is produced for core size and average shell thickness. Using statistical data from experiments done using ASAXS at Sector 15, we have determined that ASAXS produces statistically significant data about core diameter, average shell thickness, and distribution while TEM does not. During the analysis, we calculated the averages of how much the ASAXS measured values deviate from the TEM determined values. As can be seen from Table 2, the sizes collected from the ASAXS experiment were more precise and detailed than the TEM values. From NanoComposix, ASAXS analysis for the 60nm nanoparticles also showed that the density of the gold core is slightly less than the bulk density of gold which shows that the gold core within the nanoparticles has a porous structure.

Conclusions

TEM and experimental techniques are used commonly to analyze nanoparticles but ASAXS provides more detailed, statistically accurate information. The ASAXS analysis done here on two different sized silver-shelled nanoparticles has revealed similar overall sizes of the nanoparticles as the TEM measurements. However, considerable differences are obtained in terms of the core and shell sizes. The ASAXS measurements here directly show that the metrical information obtained from TEM data is not at all statistically reliable in terms of characterizing the core-shell type of nanomaterials.

Future Directions

The structural information that is gathered from the nanoparticles will help determine novel properties of the material that can be linked to the distribution of metals within the nanoparticles. Manipulating the structure and ratio of silver-coated gold nanoparticles can reveal enhanced photocatalytic, catalytic and optical properties that can advance fields such as medical care, industrial applications and catalysis.

References

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Acknowledgements

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