

Surface Characterization of Functionalized Gold Nanoparticles

Lara J. Gamble, Ali Rafati, Sirnegeda D. Techane and David G. Castner

Departments of Bioengineering & Chemical Engineering, University of Washington

Statement of Purpose: Nanoparticles require well-controlled surface properties to achieve optimum performance in complex biological or physiological fluids. However, despite the widespread appreciation of the unique properties of high surface area nanoparticles there is a surprising lack of detailed surface characterization of these materials, especially for nanoparticles used in biomedical applications. This is in part because nanoparticles present significant challenges for surface characterization. Thus, there is a need to develop rigorous and detailed surface analysis methods for characterizing the surface of nanoparticles. Model systems with well-defined, systematic variations of surface properties are an excellent starting point for developing comprehensive surface characterization methodologies. In this study the surface chemistries of carboxylic acid (COOH), amine (NH₂) and oligo(ethylene glycol) (OEG) terminated self-assembled monolayers (SAMs) functionalized Au nanoparticles (AuNPs) were characterized with X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), low energy ion scattering (LEIS), Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM).

Methods: AuNPs with average diameters of 14, 25 and 40 nm were synthesized using the Frens modified Turkevich method by heating a HAuCl₄ solution to 100°C under nitrogen and then adding a C₆H₅Na₃O₇ solution. Thiol solutions were added to the AuNP solutions to produce functionalized AuNPs with COOH, NH₂ and OEG terminated SAMs. Centrifugation and resuspension, as well as dialysis procedures, were used to purify the functionalized AuNPs. The purified AuNPs were deposited onto cleaned silicon wafers for analysis. XPS experiments were done using either Surface Science Instruments S-probe or Kratos AxisUltra DLD instruments. ToF-SIMS experiments were done using an ION-TOF V instrument. LEIS experiments were done using ION-TOF Qtac instrument. FTIR experiments were done using a Bruker Tensor 27 instrument. TEM experiments were done on a Phillips CM100 instrument.

Results: TEM showed the smallest AuNPs had a narrow size distribution (14±1 nm) and were spherical (see Figure 1). As the average size of the AuNPs increased, the size distribution increased and particles became less spherical. Experimental conditions were identified that resulted in complete SAMs forming on the AuNPs for a range of terminal groups and chain lengths. For COOH-SAM covered AuNPs, as the AuNP diameter decreased and SAM chain length increased, the XPS atomic C/Au ratio and the ToF-SIMS intensity ratio of C₁₋₄H_xO_y ions/Au-containing-ions both increased. Since the XPS C/Au atomic ratio depends on the SAM structure as well as the curved nature of the AuNPs, special XPS data analysis methods must be developed to accurately analyze SAM

covered AuNPs. Simulated Electron Spectra for Surface Analysis (SESSA) was used for this purpose. Quantities such as SAM density, thickness, surface roughness, etc. were tuned in SESSA to optimize agreement between simulated and experimental XPS compositions. The SESSA results for 16 carbon COOH-SAMs showed that the total overlayer thicknesses was 3Å thinner on the 14nm diameter AuNPs (18.5Å) compared to a flat Au surface (21.5Å). Included in the measured total overlayer thicknesses was the presence of a 1.5Å hydrocarbon contamination layer. LEIS was also used to measure the total overlayer thickness on the SAM covered AuNPs. The thickness measured by LEIS (18Å for the C16 COOH SAMs on 14nm AuNPs) was in excellent agreement with the SESSA/XPS total film thickness.

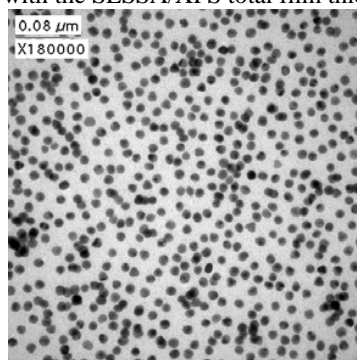


Figure 1. TEM image of the 14nm AuNPs.

Both methoxy (CH₃O-) and hydroxyl (HO-) terminated OEG SAMs with chains containing 11 methylene and 4 ethylene glycol units were examined. ToF-SIMS clearly differentiates the two OEG SAMs based on the different masses of the two terminal groups. XPS showed a significant difference between the same SAM on different sized AuNPs. Both OEG SAMs were more densely packed on the 40 nm diameter AuNPs compared to the 14 nm diameter AuNPs. FTIR experiments indicates the methylene backbone groups are well-ordered on all gold surfaces, but the OEG groups are more ordered on the 40 nm diameter AuNPs. Together the XPS and FTIR results suggest the OEG SAMs form a thicker and/or higher density SAMs on the 40 nm AuNPs compared to the 14nm AuNPs. LEIS experiments quantified this difference, showing the OEG SAMs had thicknesses of 20Å and 26Å, respectively on the 14 and 40nm AuNPs.

Conclusions: XPS and LEIS methods to quantify the overlayer thickness on AuNPs have been developed. It was determined that COOH SAMs are 3Å thinner on AuNPs compared to flat Au surfaces and have a 1.5Å adventitious hydrocarbon layer. The OEG SAMs are more well ordered and thicker on the 40nm AuNPs compared to the 14nm AuNPs.