602 CD
DOI: 10.1017/S1431927606062684
Microsc Microanal 12(Supp 2), 2006

Nanoscale Structural and Chemical Characterization of Silica-coated Gold Nanoparticles Using STEM 3D Imaging and EELS

D.N. Leonard[1], K.F. Jarausch[2], M.G. Cerruti[3], G. Duscher[1,4], S. Franzen[3], D.L. Feldheim[3]

[1] Dept. of Mat. Sci. & Eng., North Carolina State University – Box 7907, Raleigh, NC 27695-7907
[2] Hitachi High Technologies America, Inc. – 5100 Franklin Dr., Pleasanton, CA 94588
[3] Dept. of Chemistry, North Carolina State University – Box 8204, Raleigh, 27695-8204
[4] Division of Mat. Sci. & Eng., Oak Ridge National Laboratory – Oak Ridge, TN 37831

Plasmon excitation of Au nanoparticles (Au NPs) causes blackbody radiation emission which is currently being exploited to create labels for sensing applications (e.g. DNA detection assays). A new method to maximize emissivity in the IR region, using a silica encapsulated Au core NP, was tested and produced an order-of-magnitude increase in the thermography detection limits. Experimental details and results can be found in Ref. [1].

The purpose of this study was to use nano-scale characterization to probe individual silica-coated Au NPs and further understanding of local material properties of the nano-engineered sol-gel deposited silica shell. Combined STEM / EELS analysis was used to document NP morphology, confirm chemical composition of the SiO_2 and determine its electronic and optical properties (e.g. band gap, plasmon-peak energy). A Hitachi HD 2300 STEM, equipped with a 360 degree rotation holder and operated at 200 kV, was used to capture Z-contrast, bright field and SEM like topography SE images of several representative silica-coated NPs. A Gatan Imaging Filter (GIF) was used to acquire low-loss and core-loss EELS spectra as sequential line scans, with a ~1 nm diameter electron probe, across the silica shell of single NPs. EELS low-loss spectral analysis and core-loss quantitative analysis was accomplished with Gatan Digital Micrograph™ 3.10 and QuantiFit, a new approach to spectral analysis using a spreadsheet solver and macros.

Micrographs from STEM imaging, viewable on-line as animated rotation sequences, were used for 3D visualization of core-shell NP morphologies as shown in Fig. 1. The series of EELS low-loss line scans, illustrated in Fig. 2 as blue lines, acquired from single nanoparticle silica shells were analyzed after performing single scattering deconvolution. Low-loss data displayed in Fig. 3 shows a band gap of the silica shell at ~ 8.9 eV and plasmon-peak energy at ~ 25.5 eV [3]. Surprisingly, little variation of material properties were observed across the NP shell, but anomalies in the spectra did occur in regions sampled near the Au core. Quantitative EELS analysis confirmed NP silica-shells to be stoichiometric SiO_2 which is in agreement with the chemical dependent band gap energy [2]. These analytical characterization results documented the morphology and materials properties responsible for experimentally determined increases in IR emissivity found in prior thermography studies of DNA detection assays.

References:

[1] M.G. Cerruti, *et. al.,* "Gold and Silica-Coated Gold Nanoparticles as Thermographic Labels for DNA Detection." *submitted to Analytical Chemistry*.
[2] S. Schamm, *et. al.*, "Study of the dielectric properties near the band gap by VEELS: gap measurement in bulk materials." *Ultramicroscopy*, 96, (2003) 559–564.
[3] M. A. Turowski, *et. al.*, "Profiling of the dielectric function across A1/SiO2/Si heterostructures with electron energy loss spectroscopy." *Ultramicroscopy,* 41, (1992) 41-54.

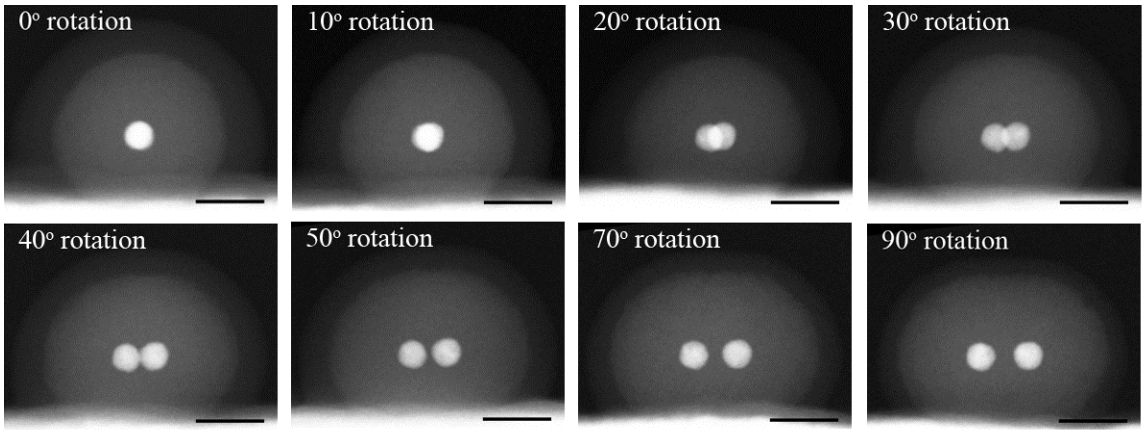

Figure. 1 STEM Z-contrast image sequence showing the appearance of a second 20 nm Au core (bright contrast) as the NP was rotated 90 degrees. Scale bar is 50 nm.

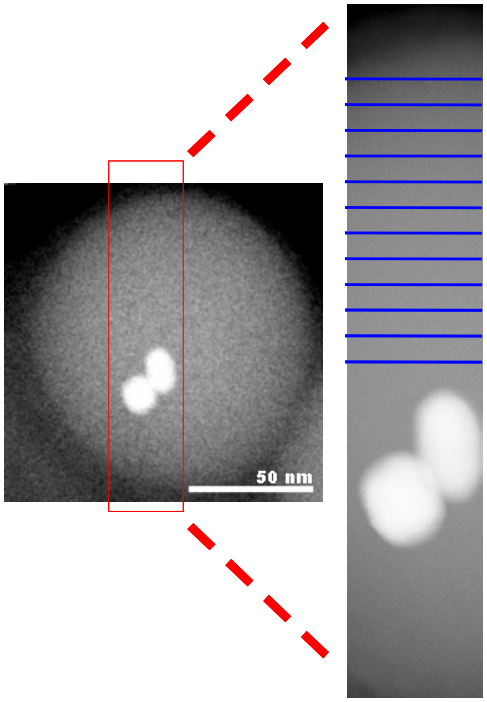

Figure. 2 The red-box outlines a reduced scan area used to collect EELS line scans (blue) across the SiO_2 shell.

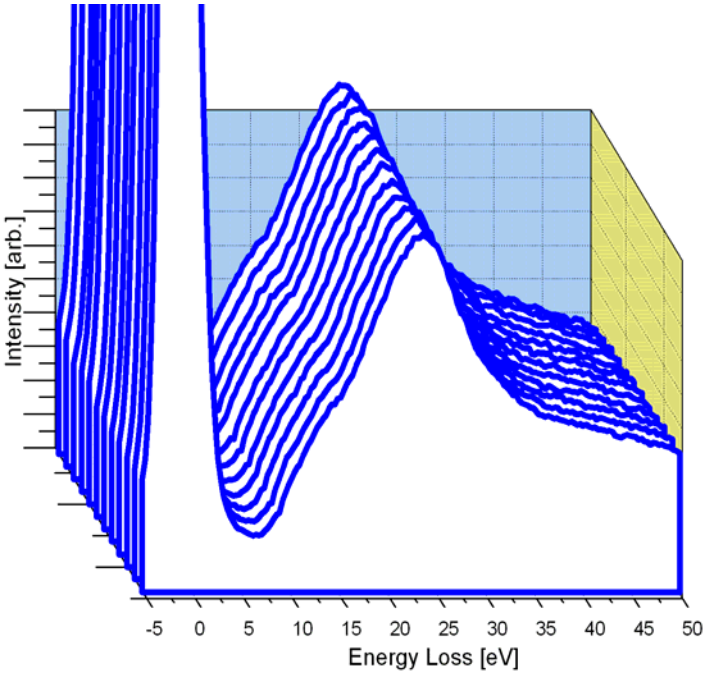

Figure. 3 Low-loss data from the 12 scans illustrated in Fig. 2. The band-gap energy of ~8.9 eV and plasmon-peak energy of ~25.5 eV do not vary significantly across the NP diameter sampled with EELS.

https://doi.org/10.1017/S1431927606062684 Published online by Cambridge University Press