

## Fast simultaneous acquisition of low- and core-loss regions in the EELS spectrum from catalyst particles containing the heavy metals Au and Pd using the GIF Quantum®

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Metals such Pd and Pt have been extensively used in the automotive industry as exhaust gas catalyst for pollution control. Until recently Au has never been used due to its thermal instability. In particular, Au particles at the nanometer scale show a melting point at relatively low temperatures that are much lower than the temperatures experienced during the catalytic process. However, Pd/Au alloys have attracted a lot of interest due to their resistance at high temperatures and this explains their use in several field such as the CO and hydrocarbon oxidation, the synthesis of Vinyl acetate monomer, hydrocarbon hydrogenation and many others. Pd is the catalytic center whereas the Au has the effect of changing the chemical properties at the surface of the Pd-Au alloy. This changes influence the catalytic properties. Hence, the study of the chemistry and the elemental distribution is important in order to understand the properties of the whole catalyst system. TEM related techniques have proved to be valuable tools for characterizing such materials.

Traditionally Pd/Au alloys or other particle systems containing high-Z elements such as Au or Pt have been mainly characterized using STEM imaging and also EDS for extracting some composition information. Historically, EELS has not generally been used for these systems since their characteristic edges in the EELS spectrum are at relatively high energy (> 1keV) which require high-brightness sources and stable instruments to record. However, analysing materials containing heavy elements using EELS would be very beneficial given the wealth of information contained in the EELS spectrum compared to only the relative composition given by EDS analysis. In addition to the simple compositional distribution which is available with both EELS and EDS, EELS can give insight into the nanoscale chemistry, bonding, optical properties and thickness/density changes of the material. This information cannot be obtained using EDS.

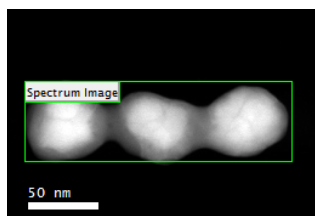


Figure 1. ADF STEM survey image. The green box is the area where the EELS SI were taken

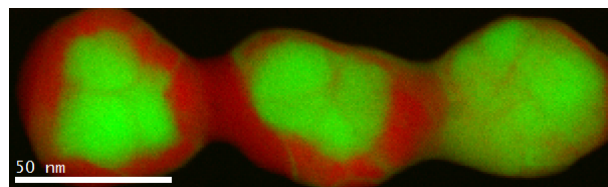


Figure 2. RGB composite image of Au/Pd nanoparticle. Au  $M_{4,5}$ -edges at 2206eV in green and Pd  $L_{2,3}$ -edges at 3173eV in Red

Green: Au  $M_{4,5}$ -edges at 2206eV  
Red: Pd  $L_{2,3}$ -edges at 3173eV

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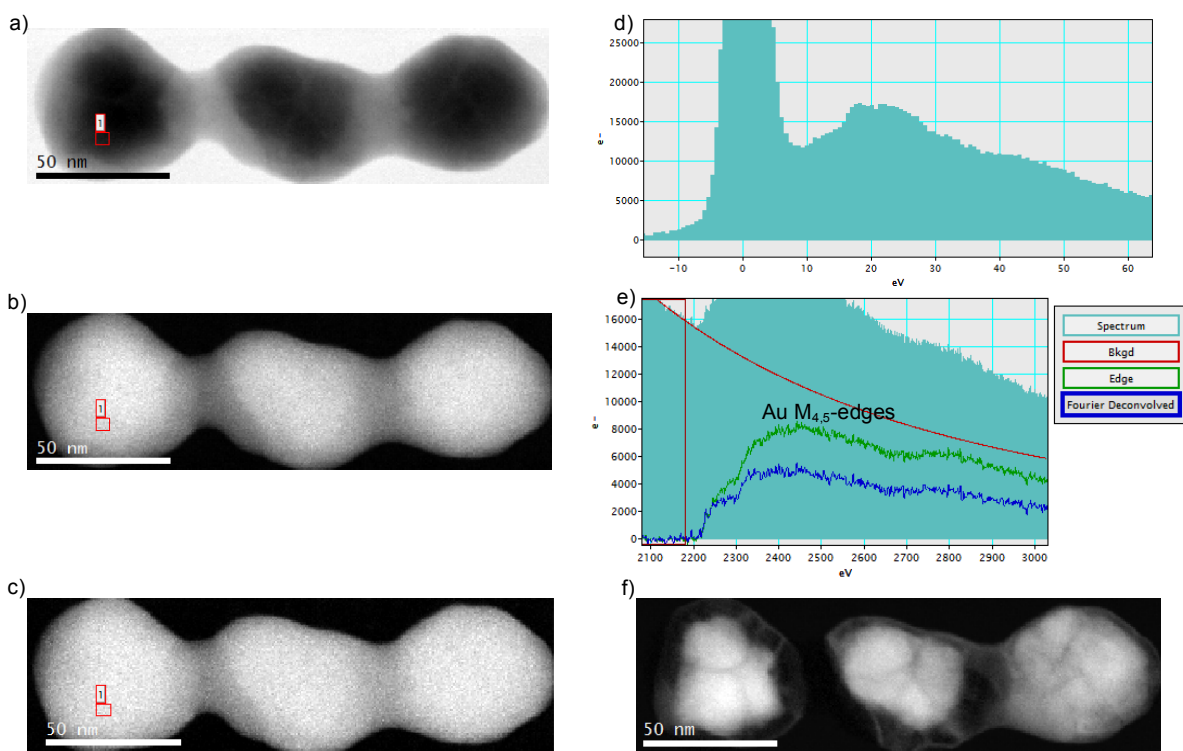
With the advancements in aberration-corrected transmission electron microscopy the resolution in scanning transmission electron microscopy (STEM) has been enormously improved. More importantly, the reduction of the probe size and the dramatic increase of the probe current lead to the capability of acquiring high resolution elemental and chemical maps using EELS at energy losses previously thought nearly impossible. With these advances, there is so much current in these sub-nanometer probes that fast EELS spectra with good signal-to-noise ratio can now be acquired from the high-energy portion of the EELS spectrum for heavy elements such as Au in just a few milliseconds. High spatial resolution EELS maps can now be easily acquired with the acquisition time to a large part limited by the speed of the EELS spectrometer. The introduction of fast EELS spectrometers such as the GIF Quantum has dramatically changed the rate that information can be recorded in a EELS Spectrum Imaging dataset. EELS maps can be acquired at over 1000 spectra per second that allows fully take advantage of the increased probe current available in an aberration probe corrected microscope. In addition, the multipole optics present in the GIF Quantum® correct the aberration up to the 5<sup>th</sup> order allowing the use of high collection angles maintaining high energy resolution. Matching the collection angle to the large STEM probe angles available today is critically important in high-energy loss experiments. Another feature available in the GIF Quantum® is the dual EELS capability that allows acquire simultaneously the low and core loss regions of the EELS spectrum under the same experimental conditions. Having the low loss region of the EELS spectrum allows the determination of the absolute number of atoms present in the sample, the correction for any multiple scattering in the sample and the accurate measurement of chemical shifts due to variations in the local chemistry. In addition, optical excitations that are confined in the low-loss region of the EEL spectrum are available for analysis. This has been critically in understanding surface plasmon effects in metallic nanoparticles for example.

Au/Pd nanoparticles sample was provided by Professor Jianfang Wang's Group at the Chinese University at Hong Kong. Data was acquired using a probe corrected FEI Titan Cubed 80-300 equipped with a high-brightness X-FEG electron source and a Gatan GIF Quantum® ERS as EELS spectrometer. EELS data was acquired in STEM mode using a ~0.2nm probe containing over 200pA of current. The probe convergence angle was 25mrad and the collection angle over 100mrad. The actual collection angle was not directly measured but estimated based on the microscope camera length and the EELS spectrometer entrance aperture used for the experiment. EELS SI analysis was carried out in DualEELS™ mode and the regions of the EELS spectrum from 0eV to 2000eV and 1800eV to 3800 were simultaneously acquired using acquisition times of 50µs and 49ms respectively. Therefore, the total acquisition time per each pixel was way less than 50ms with better than 94% live time. Taking advantage of the fast acquisition mode available in the GIF Quantum® and the increased probe, over 55000 spectra (396x91x2) were acquired with the total acquisition time of just over 25minutes from a very wide region as shown in Figure 1. The pixel size was 0.6nm giving a slight under sampling of the data given the ~0,3nm probe. Additional performance would have been achieved by increasing the probe size (the current) to better match the pixel size. The EELS SI data was acquired without any spatial drift correction applied showing the high stability of this microscope installation. Figure 2 shows the RGB map of the sample composition extracted from the Au M<sub>4,5</sub>-edges at 2206eV and the Pd L<sub>2,3</sub>-edges at 3173eV. Despite the high energy edges involved, the contrast in the RGB map is very high and clearly shows where Pd and Au are localized with great detail. This is due to the large cross-section for these edges, the low background at high energy losses and the inherent local nature of the EELS scattering process. The EELS signal can only be generated at the position of the electron beam and never from secondary scattering fluorescence from other areas of the sample.

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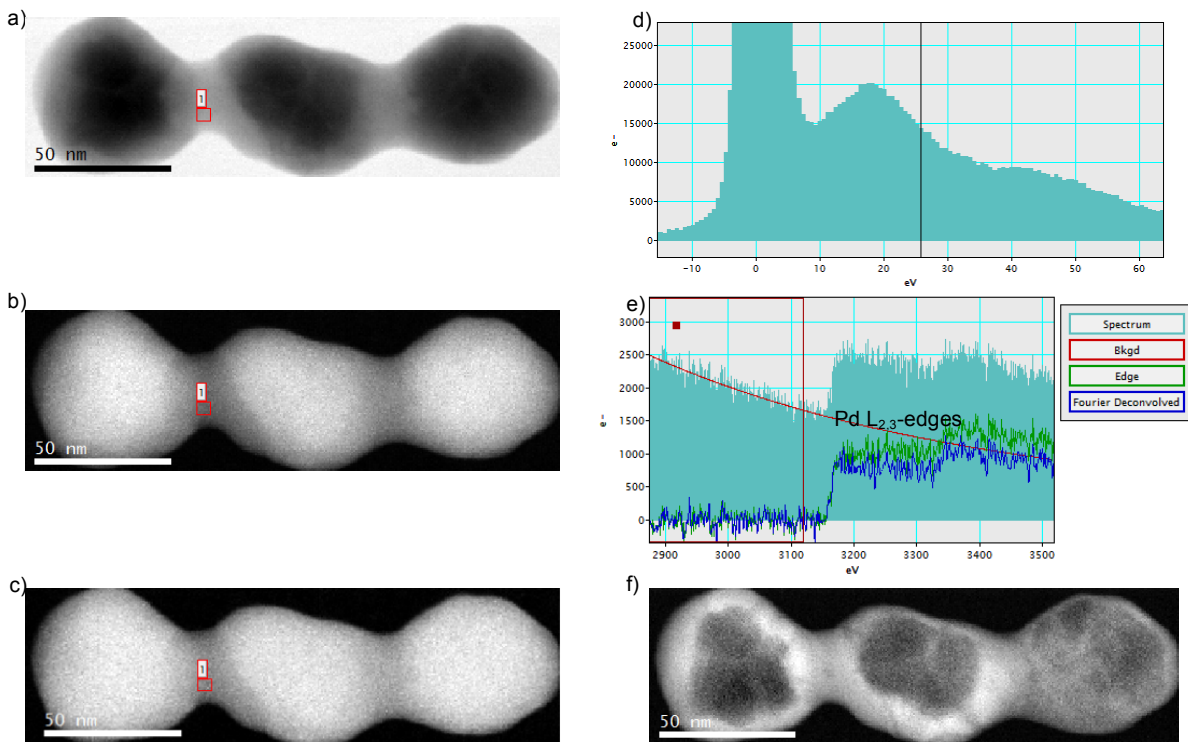
As indicated above, data was acquired in Dual EELS™ mode. In this way, it is possible to have the information from the low loss region of the spectrum that allows get the information provided by the plasmon along with the zero loss (ZL) peak in the same dataset. Plural scattering in the Au  $M_{4,5}$ -edges and the Pd  $L_{2,3}$ -edges can now be deconvolved to obtain the single scattering contribution. This is shown in Figures 3 and 4. Given the zero-loss and low-loss portions of the spectrum, the absolute thickness for the whole particle can be obtained as shown in Figure 5.

Concluding this application paper, fast atomic EELS maps with high contrast can now be acquired with a good signal-to-noise ratio. Using the GIF Quantum in DualEELS mode allows the simultaneous acquisition of two different regions of the EELS spectrum. In the case of this paper, the low- and the core-loss regions of the EELS spectrum were acquired. This is very beneficial as additional information can be obtained. It is also possible to acquire two regions in the core-loss portion of the EELS spectrum containing the Au  $M_{4,5}$ -edges at 2206eV and the Pd  $M_{4,5}$ -edges at 335eV respectively.



Figures 3. 3a) EELS SI from the low loss region; 3b) EELS SI from the core loss region; 3c) EELS SI from the core loss region deconvolved; 3d) EELS spectrum extracted from the low loss region; 3e) EELS spectra before and after deconvolution. The contribution from the multiple scattering is evident; 3f) Au  $M_{4,5}$ -edges elemental map

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Figures 4. a) EELS SI from the low loss region; b) EELS SI from the core loss region; c) EELS SI from the core loss region deconvolved; d) EELS spectrum extracted from the low loss region; e) EELS spectra before and after deconvolution. The contribution from the multiple scattering is evident; f) Pd L<sub>2,3</sub>-edges elemental map

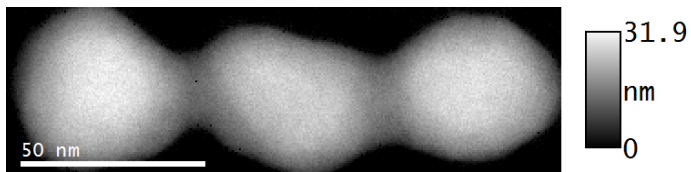


Figure 5. Absolute thickness map obtained using the low loss region of the EELS spectrum available under the same conditions in the same dataset