

Fast STEM EELS Spectrum Imaging analysis of Pd-Au based catalysts

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The latest generation of EELS spectrometers, such as the GIF Quantum and the Enfinium, are equipped with a camera that, as a result of the largely improved duty-cycle [1], is so sensitive that EELS spectra from heavy elements such as the Au and the Pt can be acquired in a matter of milliseconds. Furthermore, the extended dynamic range that can be obtained using the DualEELS capability [1,2] to simultaneously acquire two different energy regions of the EELS spectrum allows the collection of a broad range of EELS edges at high SNR over the entire energy range [1,2].

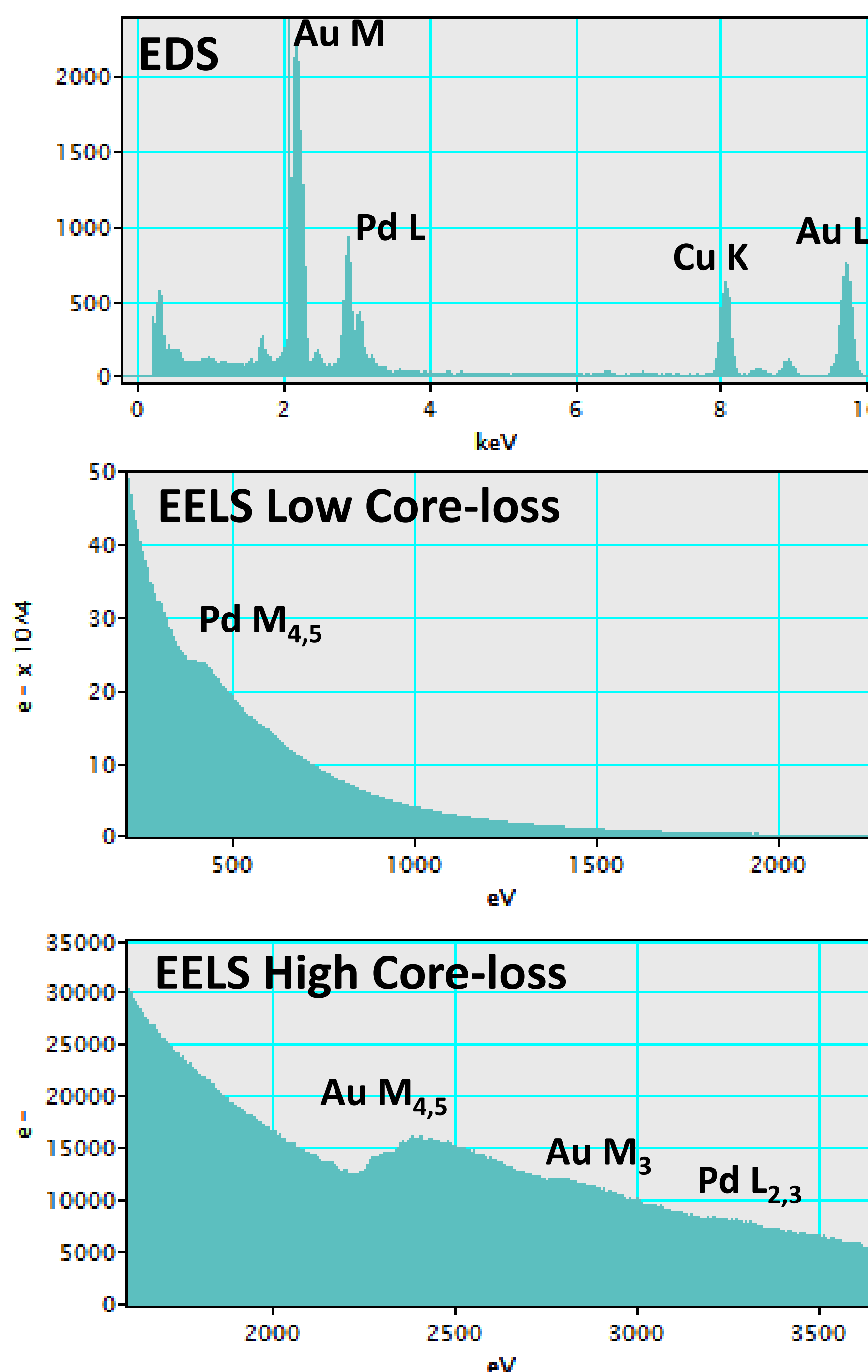
To illustrate these advances, data were acquired from catalyst samples using a GIF Quantum ERS EELS system at FELMI, TU-Graz in Austria. The TEM used was a probe corrected FEI Titan G2 STEM equipped with X-FEG high-brightness electron source operating at 300kV. The microscope is also equipped with 4 quadrant SDD detector (FEI Super-X) controlled by the Bruker Esprit system. The sample analysed contained Pd-Au catalyst nanoparticles deposited on a carbon film supported on a Cu mesh TEM grid.

EELS data were acquired in DualEELS mode and the regions of the EELS spectrum from 200eV to 2200eV and 1800eV to 3800eV were acquired using acquisition times of 7ms and 30ms respectively with a probe current of 220pA. EDS spectra were acquired simultaneously, integrating counts over the entire pixel time employed for the DualEELS spectrum. EELS and EDS data were acquired using DigitalMicrograph with a hardware synchronized joint EELS/EDS system firstly developed in Graz and described in [3]. Figures 1a,b,c show EDS and high and low core-loss EELS spectra after summing multiple adjacent pixels across the region between two particles.

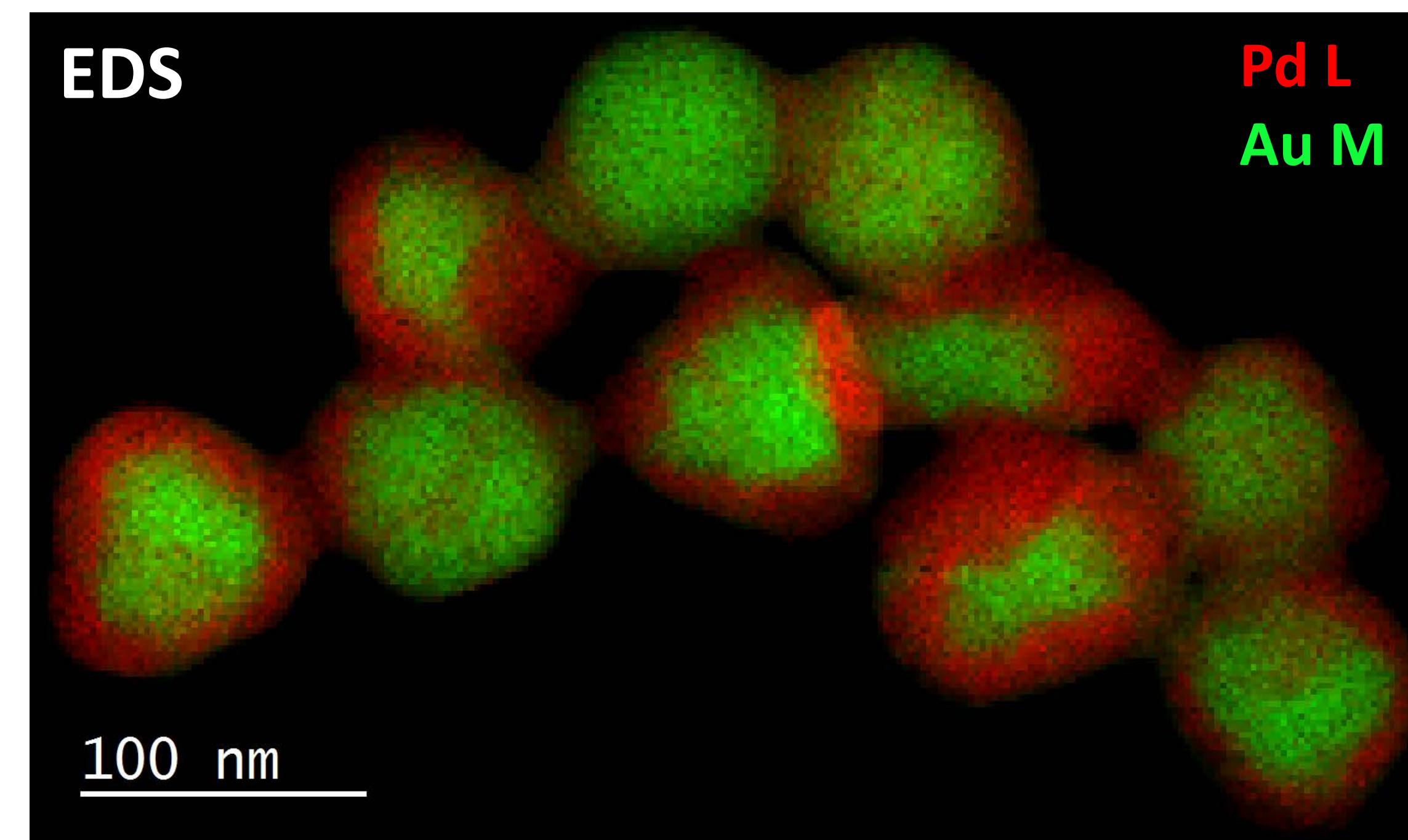
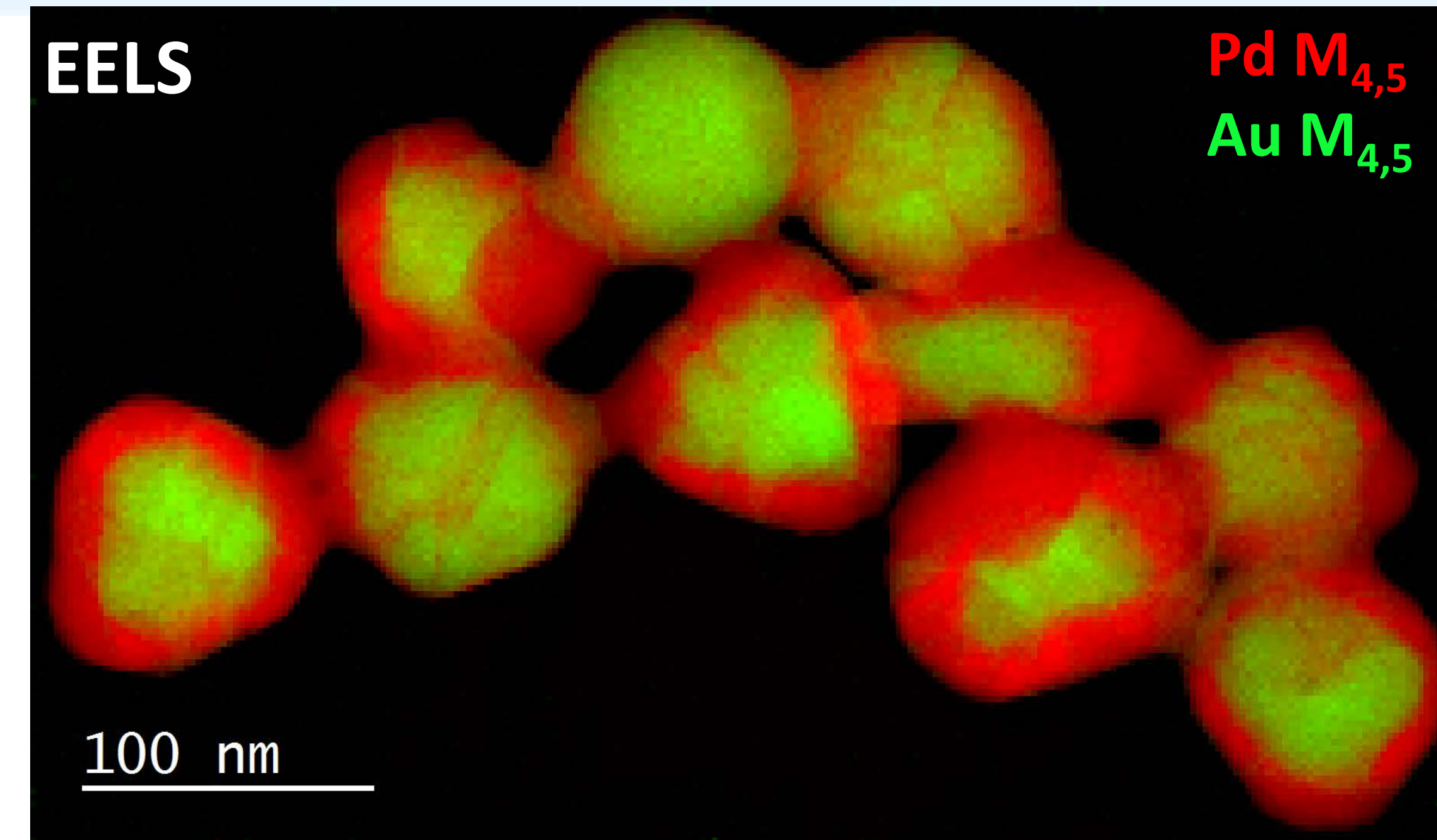
In the summed EDS spectrum the lines for all the elements expected to be present in the sample are observed. In additions, spectral lines from the Cu and Fe are observed. The lack of the Cu and Fe $L_{2,3}$ -edges at 931eV and 708eV in the EELS data verifies the artifact nature of the EDS signal. Qualitatively the EELS maps as shown in Figures 2,3,4 appear to be sharper and show much higher contrast. In particular, significant details are absent in the EDS maps which are clear in the EELS maps. For example, the diffusion of the Pd into the Au region is below the noise level of the EDS maps whereas this is clear in the EELS.

DualEELS data at 300kV from a PtRu catalyst nanoparticle are also shown and were acquired at McMaster University, Hamilton, Canada using a similar microscope installation to what described above for the experiment carried out in Graz. However, there was no EDS detector to compare with the EELS results.

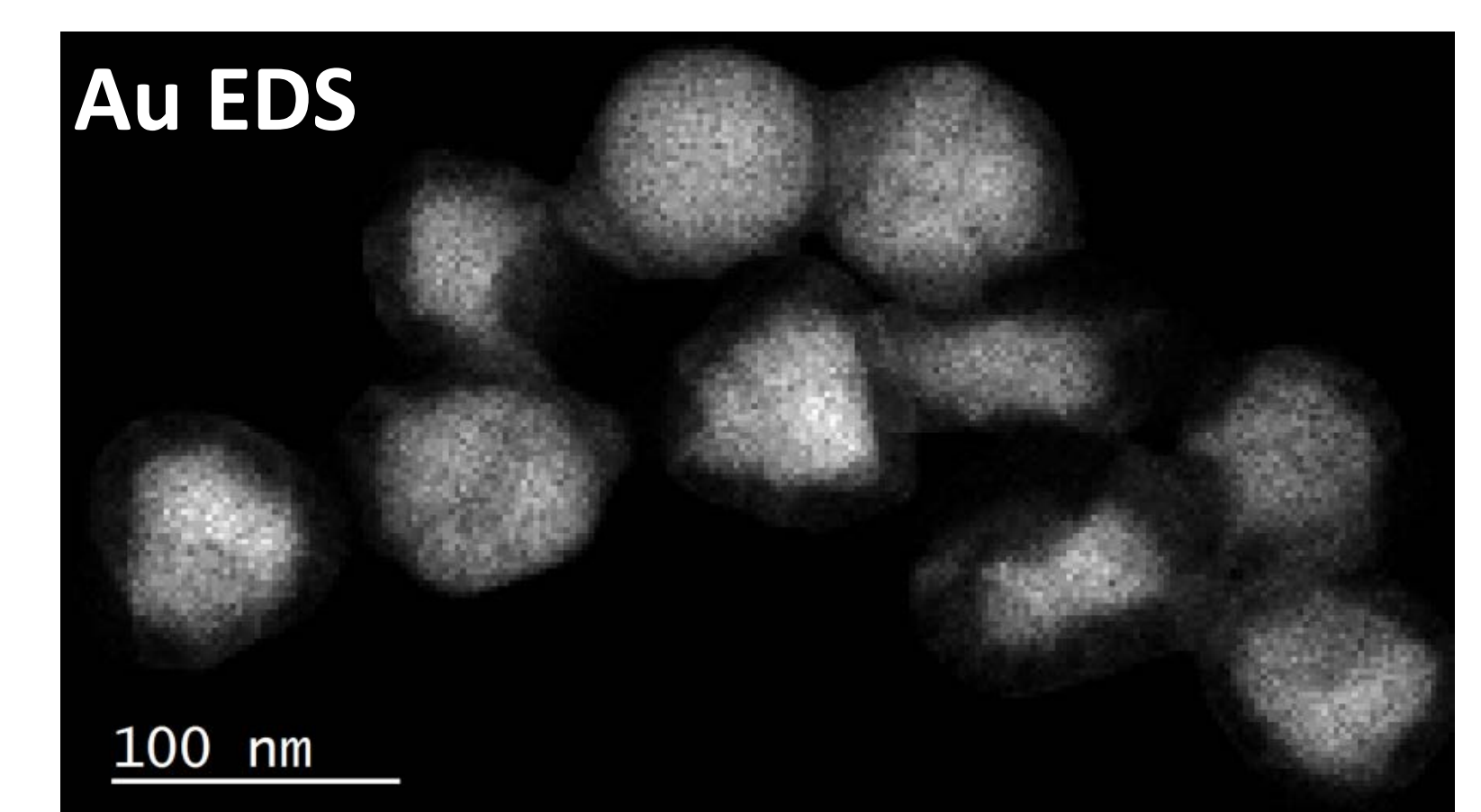
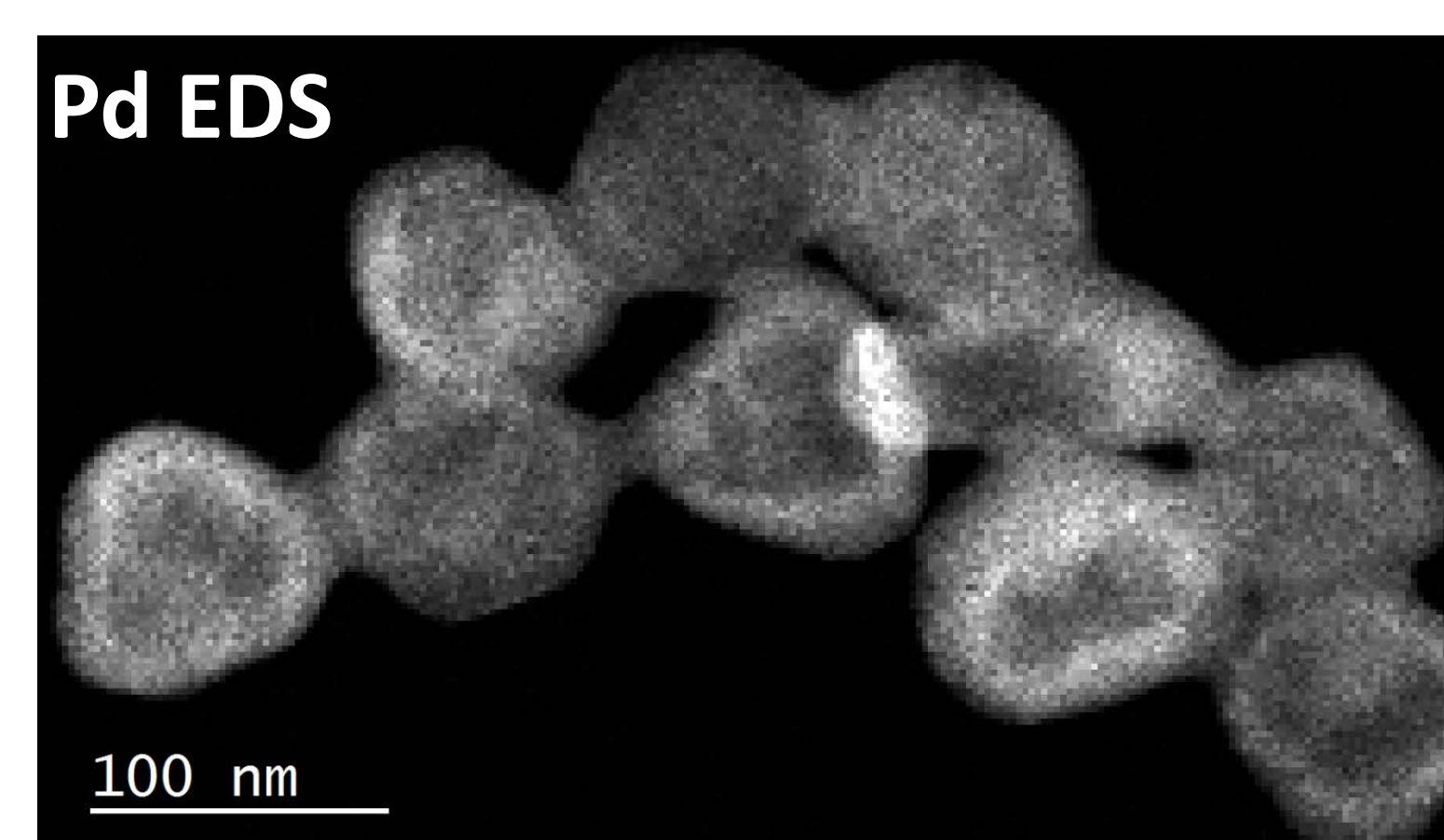
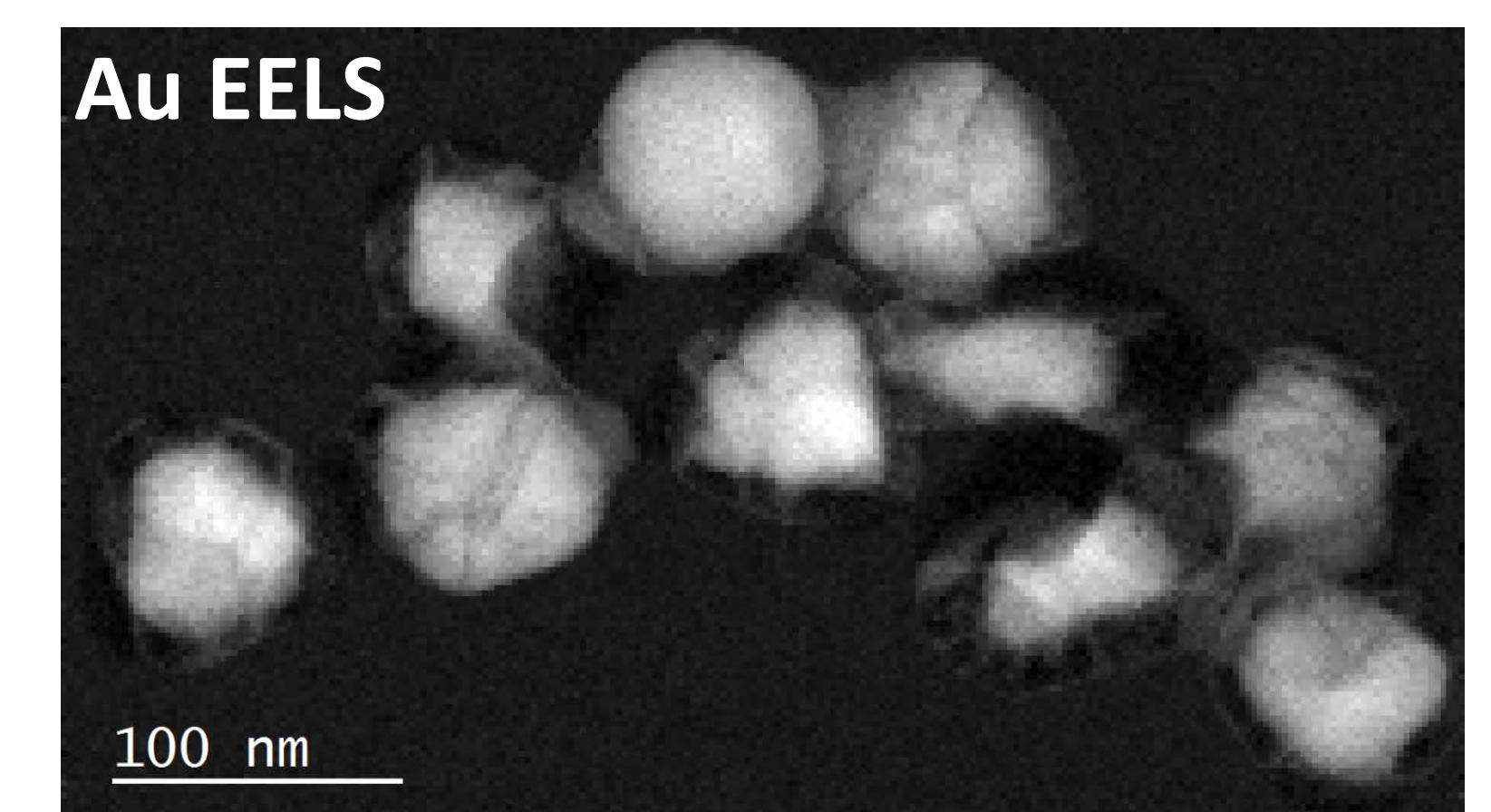
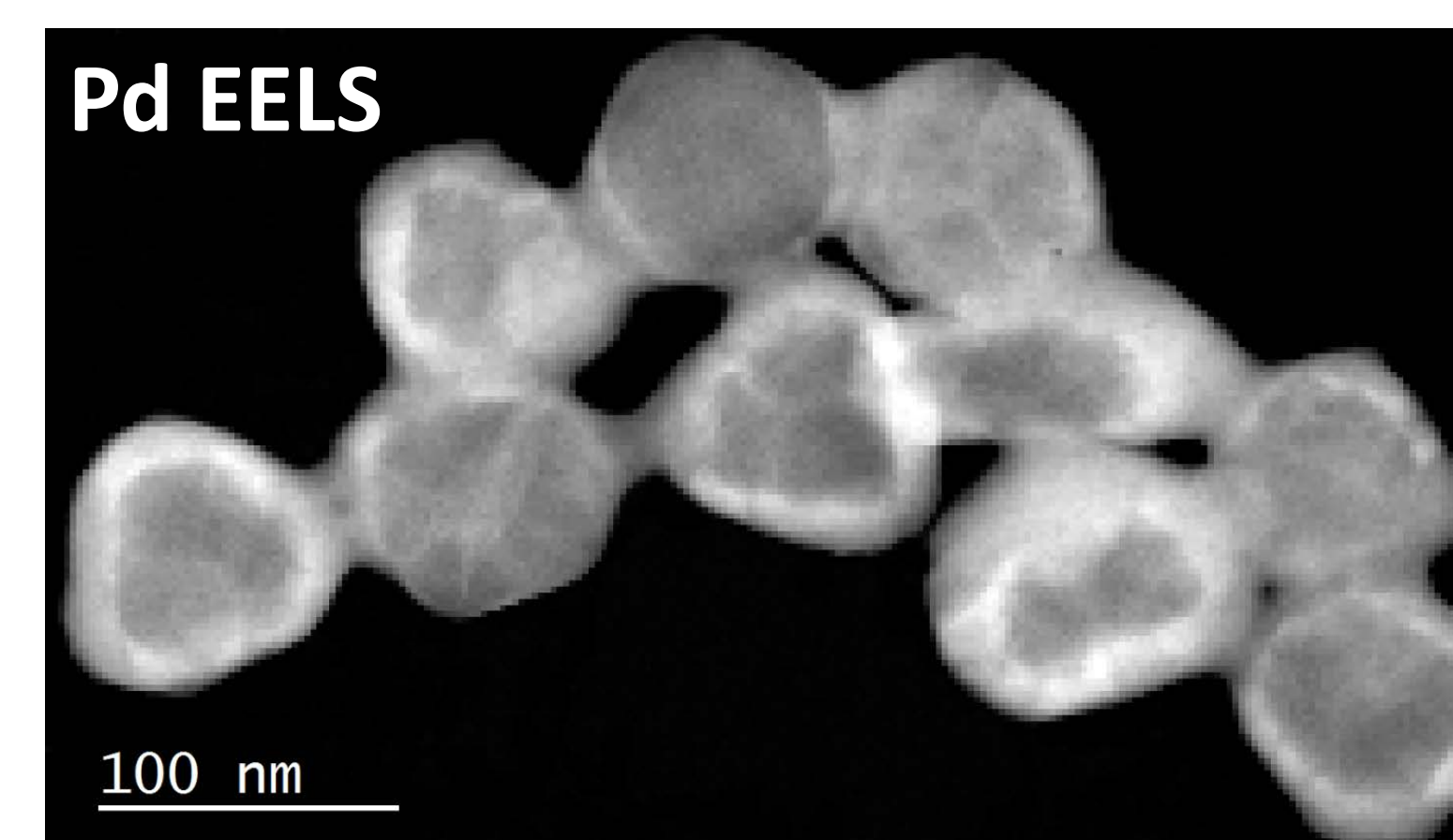
The results shown here from both the PdAu and PtRu catalyst nanoparticles demonstrate that when the EELS system and STEM are properly configured, high-energy edges can be recorded with high signal-to-noise ratio using short exposure times. This illustrates the suitability of EELS as a technique to analyze materials containing heavy metals such as Au and Pt or high energy edges in the case of the Ru $L_{2,3}$ -edges at 2838eV



Figures 1: Extracted EDS and EELS spectra summed from the same 168 pixel region at the web between two main particles; a) EDS data; b) low core-loss region from 200eV to 2200eV from the same point; c) high core-loss region from 1800eV to 3800eV. The EDS data show Cu from the nearby grid support.



Figures 2: Colorized elemental maps of Pd in red and Au in green acquired using EDS and EELS. The high signal-to-noise ratio of the EELS data results in maps sharper and show more detail.



Figures 3: Pd Elemental maps: a) EELS using the $M_{4,5}$ -edges at 335eV b) EDS using the L_{α} line at 2.84keV

Figures 4: Au Elemental maps: a) EELS using the $M_{4,5}$ -edges at 2206eV b) EDS using the $Au M_{\alpha}$ line at 2.12keV

References

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- [2] J Scott, P Thomas, M Mackenzie, S Mcfadzean, AJ Craven and WAP Nicholson, Ultramicroscopy, vol. 108, pp 1586-1594, 2008
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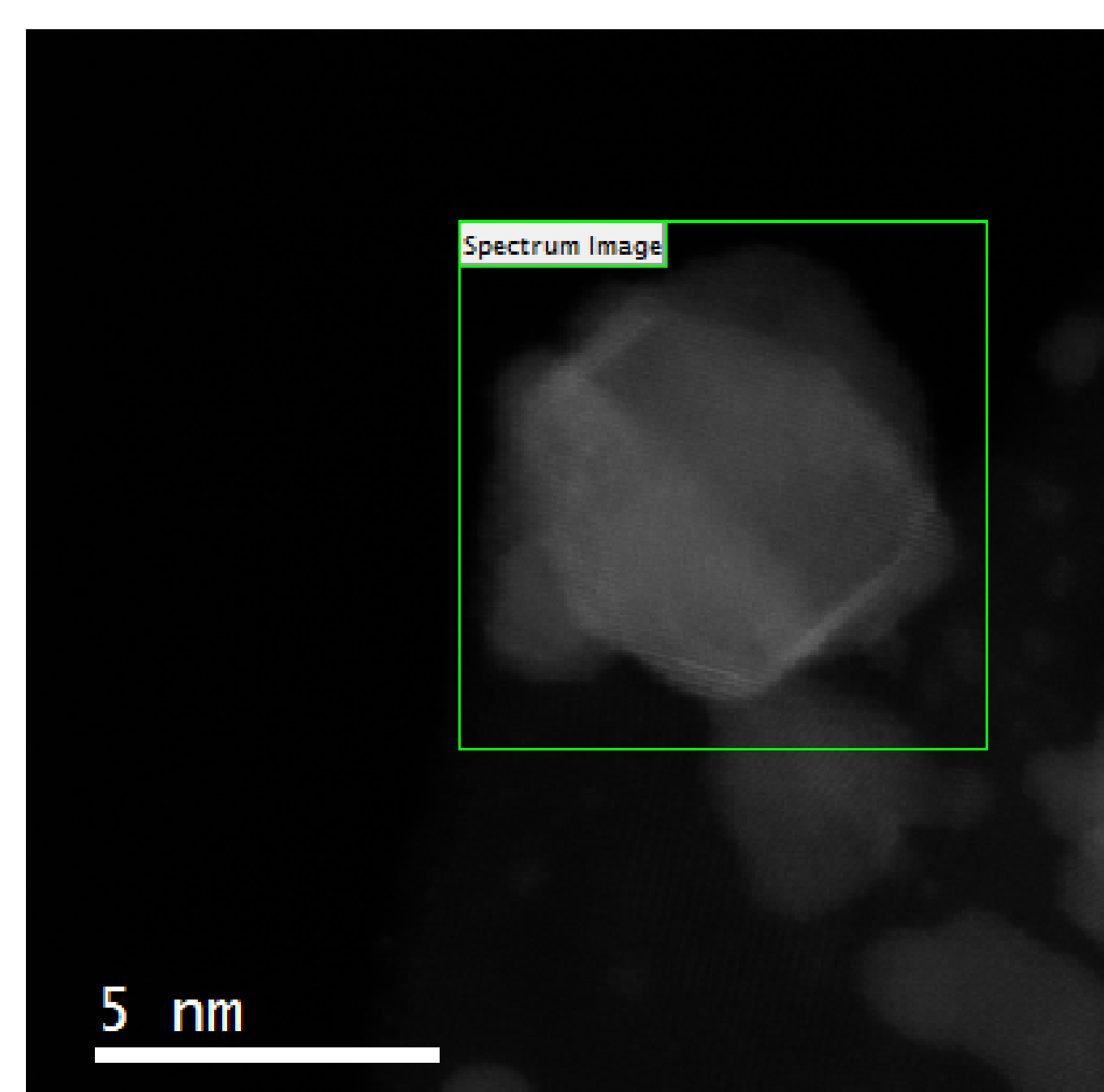


Figure 5: ADF STEM survey image. The green box is the area of the sample where the beam was scanned during the acquisition of the EELS spectrum imaging. The PtRu nanoparticle is grown on a TiO_x support.

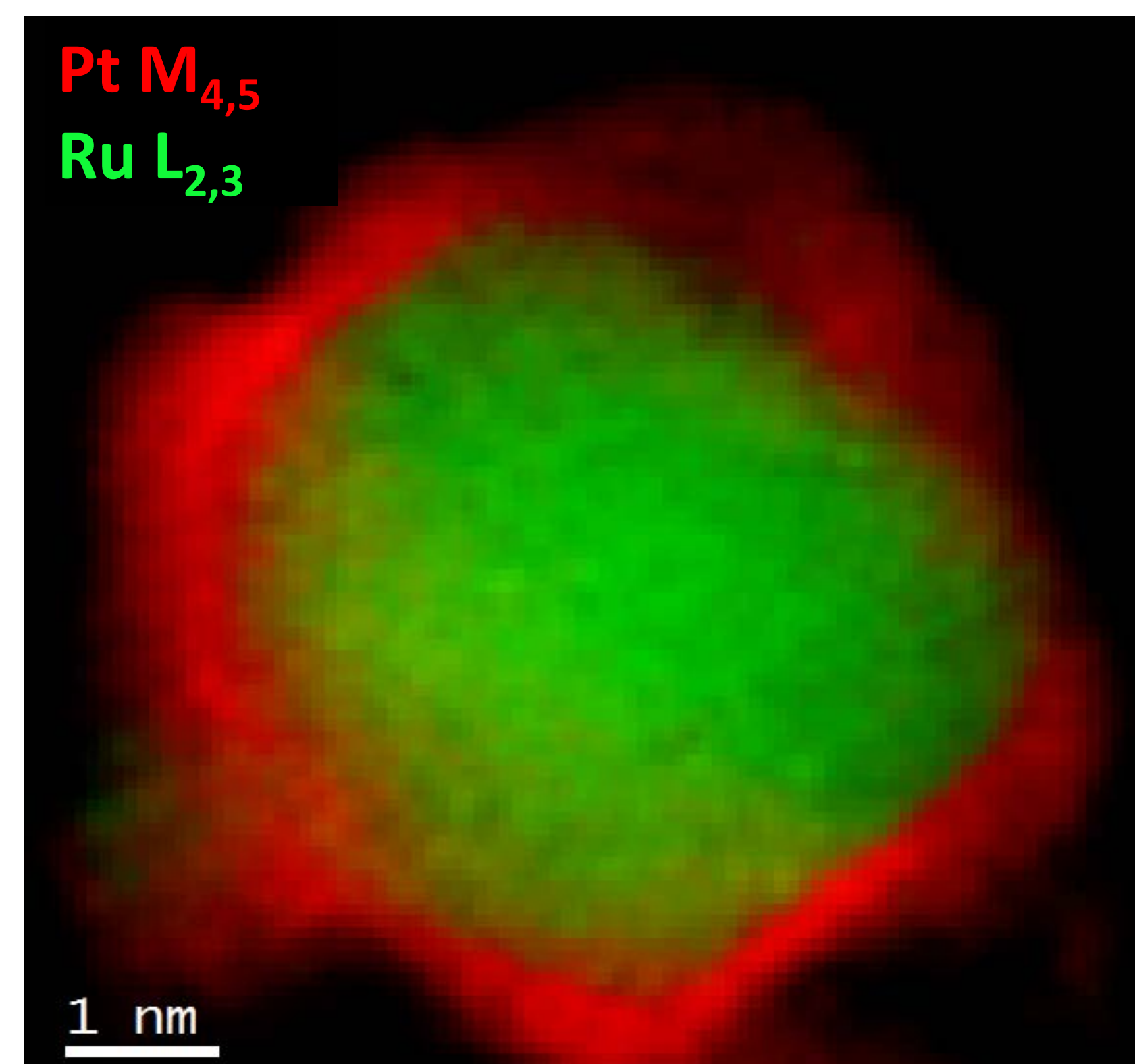
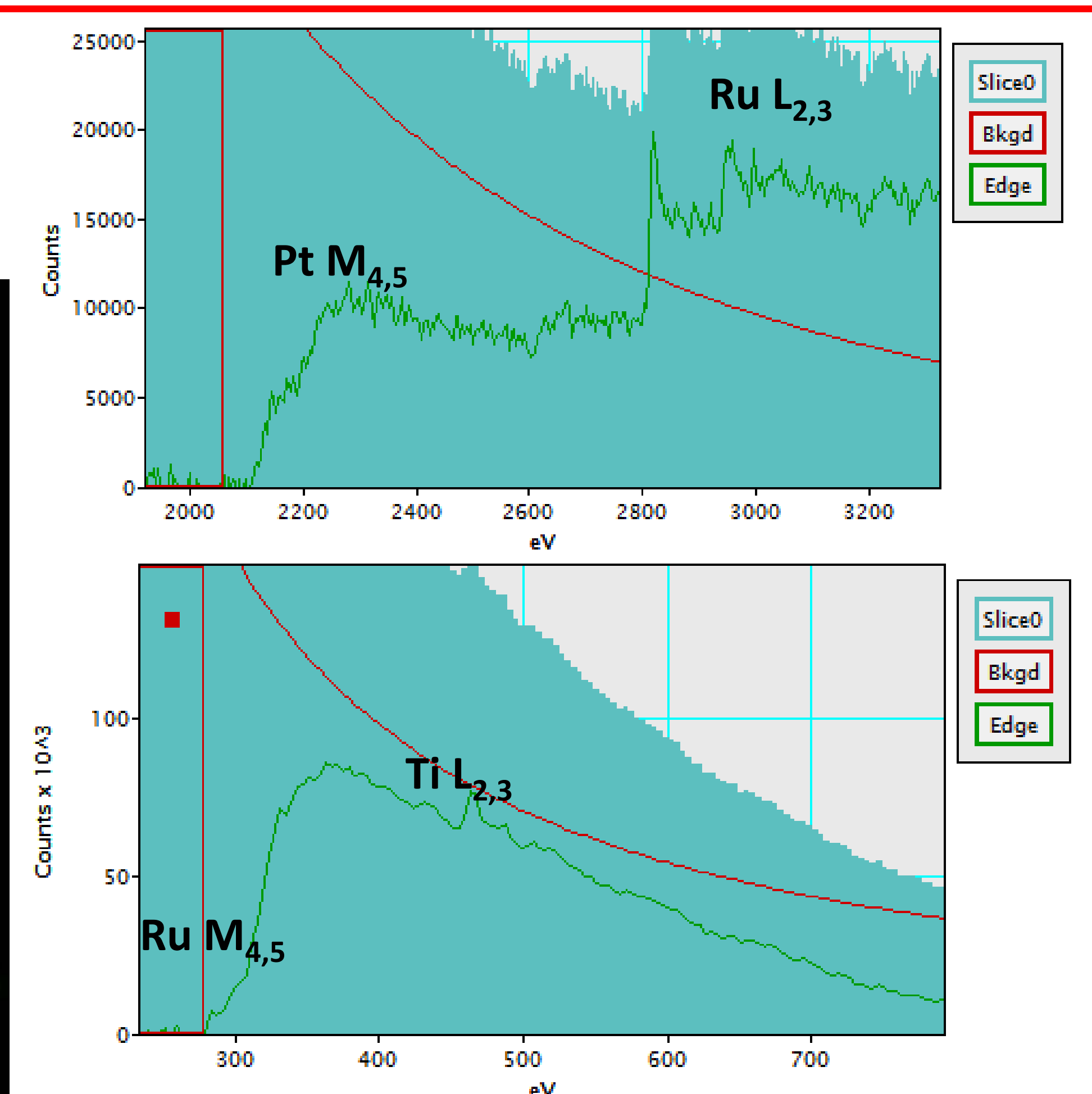


Figure 6: Colorized elemental EELS maps of Pt in red and Ru in green acquired using the $Pt M_{4,5}$ -edges at 2120eV and the $Ru L_{2,3}$ -edges at 2838eV.



Figures 7: Extracted EELS spectra across the region in proximity of the shell; a) high core-loss region from 1500eV to 3500eV acquired with an exposure time per pixel of 18ms; b) low core-loss region from 230eV to 2230eV acquired with an exposure time per pixel of 1ms. The Ru map was extracted using the $L_{2,3}$ -edges at 2838eV because of the more stable background due to the higher signal-to-background ratio SBR

