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Radial Concentration Profile Reconstruction from EDX Mapping of Au-Pt Nanoparticles

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The high spatial resolution and elemental sensitivity of energy-dispersive X-ray spectroscopy (EDX) in a scanning TEM make it a method of choice for the analysis of nanostructures. Unless tomography can be applied, the internal structure of the sample must usually be deduced from through-thickness measurements. Under axisymmetric conditions provided by objects such as nanowires or nanoparticles (NPs), however, radial concentration profiles can be retrieved from the projection using an inverse Abel transform. There have been a variety of techniques developed in many areas of physics to perform a numerical inverse Abel transform to retrieve the radial profile projection. Here, we apply this technique based on EDX measurements from Au-Pt NPs having a core-shell configuration ($\mathrm{Au_{core}Pt_{shell}}$) to test two reconstruction approaches and to retrieve the radial profile of an annealed $\mathrm{Au_{core}Pt_{shell}}$ NP. The first approach, referred to as the “Numerical” method, is based on a recurrence relationship derived from reducing the inverse Abel transform to a convolution integral [1] and the second technique, referred to as the “Splines” method, solves analytically a series of cubic splines fitted to the data [2].

A drop of a colloidal solution of $\mathrm{Au_{core}Pt_{shell}}$ NPs [3] having a ~16 nm Au core diameter surrounded by a ~3 nm thick Pt shell was left to dry on a silicon nitride-coated TEM Ni grid. The NPs-loaded TEM grid was then annealed under at 600°C for 3 hours, cooled to room temperature and subsequently heated at 400°C for 3 hours. Data cubes (where each pixel contains the EDX spectrum) of NPs before and after annealing were acquired with a JEOL 2010F field-emission microscope operating at 200 kV in scanning mode and equipped with a Si-Li ultrathin window X-ray detector (Oxford Instruments Inca software). The data cube was exported to Digital Micrograph (GMS version 1.5.0) where the pixels equidistant from the center of the NP were summed to increase the signal (Fig. 1). This data reduction method is preferable to binning neighbouring pixels since a spherical symmetry can be assumed for NPs under study. The background was then removed from each of the summed spectra using a top hat filter and quantification was performed by multiple least-square fitting a set of DTSA-simulated standards [4]. The projected Au profiles with corresponding standard error are plotted for an $\mathrm{Au_{core}Pt_{shell}}$ NP (Fig. 2) and for the annealed Au-Pt NP (Fig. 3).

The reconstructed radial Au concentration profiles were calculated for the $\mathrm{Au_{core}Pt_{shell}}$ (Fig. 4) and the annealed NP (Fig. 5) using the Splines (thin line) and the Numerical (bold dashed line) methods. While the Splines reconstruction profile is smoother than the Numerical one, potential artefacts can arise from smoothing the original data. Both reconstruction schemes fail at the endpoints and discontinuities as a result of numerical artefacts and the small number of data points available. Nevertheless, both methods reproduced the position of the Au-Pt interface of the core-shell NP at ~8 nm from the NP center and preserved an average Au content close to 1.0 within the Au core. For the homogenized Au-Pt NP, the Splines technique yielded a much smoother solution than the numerical one. Indeed, given the recursive nature of the Numerical method, any random fluctuation of the NP will invariably be amplified towards the center of the reconstructed profile.

As a final remark, the reconstruction techniques are likely to fail in the case where small internal fluctuations in large NPs are dampened by the projection. Furthermore, NPs < ~10-15 nm may not generate enough signal nor sampling points to perform a reliable reconstruction. In the latter case, these problems can be overcome in some situations by applying the technique to EELS signals.

References

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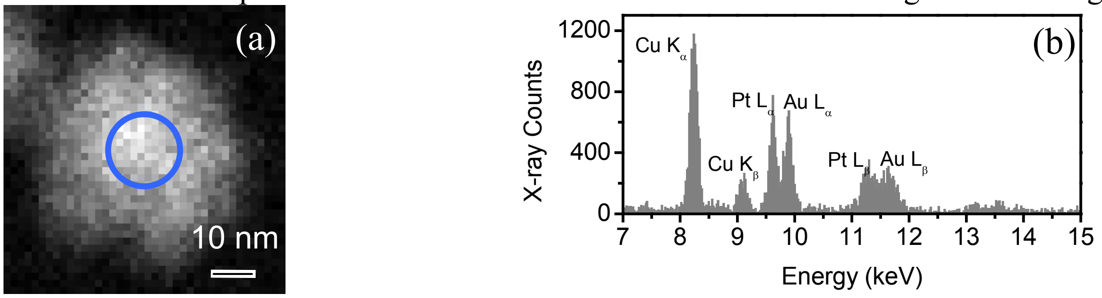

Fig. 1. Slice (a) of EDX data cube of $Au_{core}Pt_{shell}$ nanoparticle (NP). Map sampling corresponds to the pixel size of ~ 0.8 nm. Spectra covered by the annulus centered on the NP are summed in (b).

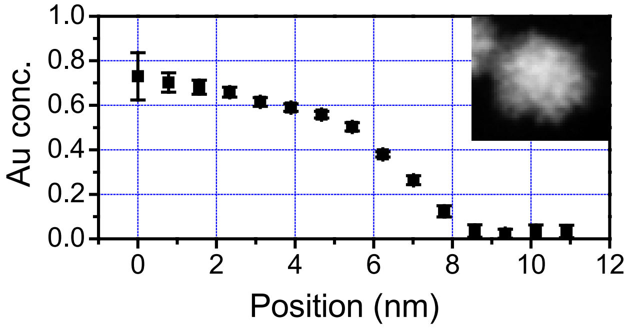

Fig. 2. Projected radial Au concentration profile of $Au_{core}Pt_{shell}$ nanoparticle (inset).

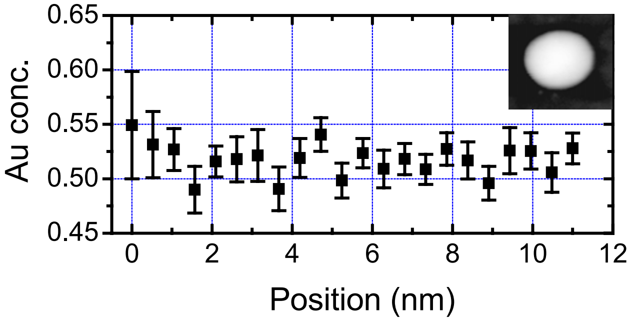

Fig. 3. Projected radial Au concentration profile of annealed $Au_{core}Pt_{shell}$ nanoparticle (inset).

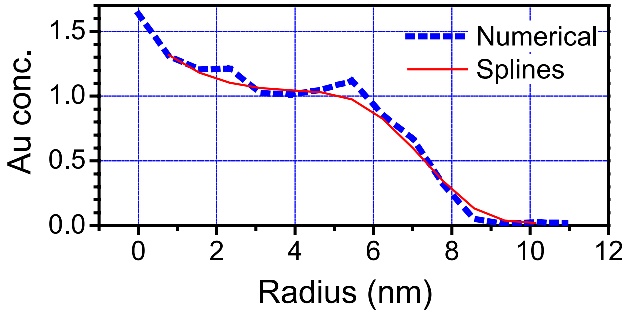

Fig. 4. Reconstructed radial Au concentration profile of $Au_{core}Pt_{shell}$ nanoparticle.

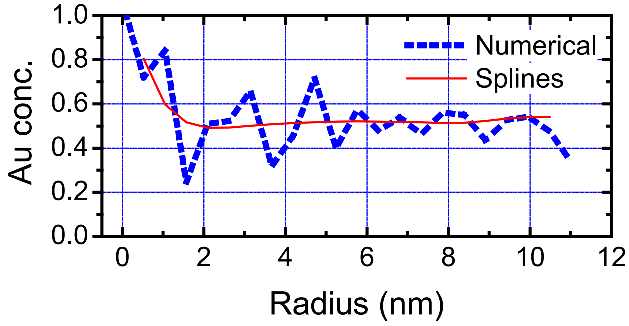

Fig. 5. Reconstructed radial Au concentration profile of annealed $Au_{core}Pt_{shell}$ nanoparticle.