Quantitative STEM of Catalyst Nanoparticles with Simultaneous ADF Imaging and Spectroscopy

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The activity of a catalyst nanoparticle is primarily affected by its size, shape, surface-strain and composition. However, the link between activity and morphology is not well understood. To understand this link, a simultaneous measurement of the size, shape, surface-strain and composition is required from an ensemble of nanoparticles. With Scanning Transmission Electron Microscopy (STEM) it is possible to measure these parameters simultaneously from a nanoparticle. The Annular Dark Field (ADF) image can be used to obtain atomic positions [1], whereas Energy Dispersive X-ray Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS) can prove high resolution compositional information. With careful instrument calibration, these signals can be recorded and quantified simultaneously using scattering cross-sections [2,3], Figure 1.

With the use of scattering cross-sections to quantify ADF, EDS and EELS measurements, it is possible to convert the measured signal from a sample into number of atoms. Such atom counts can then be modelled into three-dimensional structures. As an example, we present results of pure Pt industrial catalysts modelled from experiment images into three-dimensional structures and used as inputs for DFT. These calculations reveal the effect of surface atomic-roughness on the local electronic density. By calculating the surface averaged binding energy of a nanoparticle, it is possible to link parameters such as coordination number or particle size to catalytic activity [4].

Building on previously published methods [3,5], a methodology of quantifying spectroscopic signals as experimentally measured spectroscopic cross-sections is presented. Using these cross-sections results combining simultaneously acquired ADF, EDS and EELS signals for Pt-Co binary alloy nanoparticles will be presented, Figure 2. With this multivariate dataset it is possible to analyse changes in composition at the core and shell of nanoparticles as a function of size and thus link individual particle properties to whole ensemble properties. Finally, some preliminary multiframe spectroscopy of nanoparticles is presented showing atomic resolution in the spectroscopic mapping, Figure 3. Post-acquisition inspection allows for only those frames with minimal damage from the electron beam to be included in the quantification, further improving experimental precision and reliability [6].

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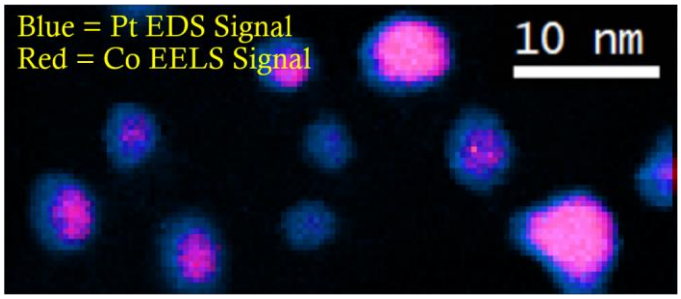

Figure 1. Composite spectroscopic map of Pt-Co alloy nanoparticles where the Pt signal was acquired using EDS and the Co signal was acquired using EELS.

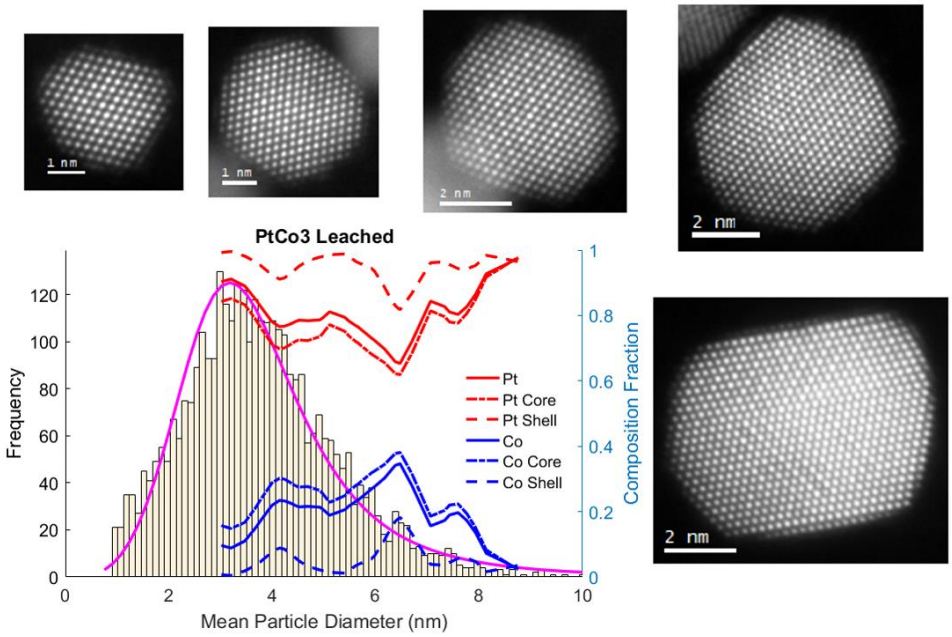

Figure 2. Quantitative characterisation of bimetallic Pt-Co alloyed nanoparticles. The fractional composition plots, overlaid on the size histogram, shows how the smaller and larger nanoparticles trend towards pure element structures.

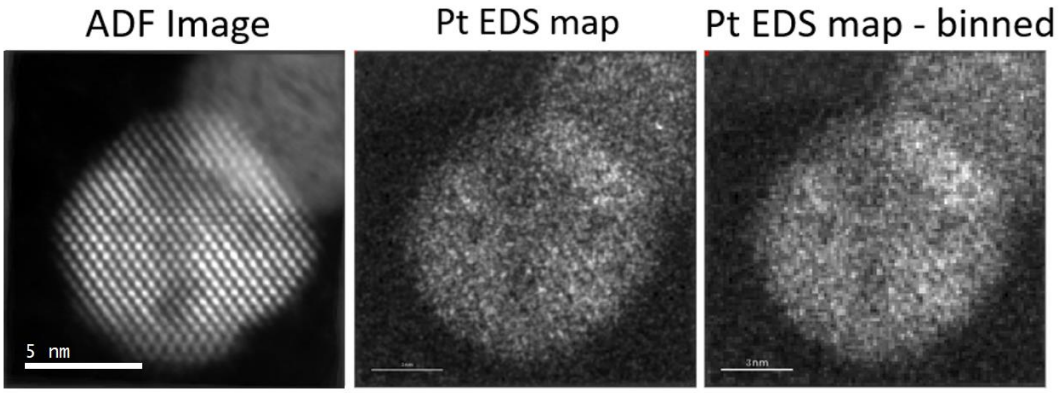

Figure 3. Simultaneously acquired on-axis ADF and EDS signals from a Pt-Co alloyed nanoparticle. The spectrum image was spatially binned by a factor of two to improve SNR.