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From High-precision Imaging to High-performance Computing: Leveraging ADF-STEM Atom-counting and DFT for Catalyst Nano-metrology

Lewys Jones[1], Chris-Kriton Skylaris[1], Peter D. Nellist[1], Aakash Varambhia[1], Jolyon Aarons[2], Katherine E. MacArthur[3], Dogan Ozkaya[4] and Misbah Sarwar[4].

[1.] Department of Materials, University of Oxford, Parks Road, UK.
[2.] School of Chemistry, University of Southampton, Highfield, UK.
[3.] Ernst Ruska Center, Forschungszentrum Jülich GmbH, Jülich, Germany.
[4.] Johnson Matthey Technology Centre, Sonning Common, Reading, UK.

Z-contrast imaging in the scanning transmission electron microscope (STEM) is a powerful tool to image precious metal heterogeneous catalysts at the atomic scale. When the annular dark-field (ADF) images from the STEM are quantified onto an absolute scale (Figure 1), it has been shown that it is possible to count the number of atoms in individual atomic columns of metallic nanoparticles and to estimate their three-dimensional structure [1]. In recent years further progress has been made in identifying the possible sources of error in the recording and analysis of quantitative annular dark-field (ADF STEM) images [2], in experiment-design, and in verifying the metrology by tomographic techniques. Of these developments, the move to fast multi-frame image-acquisition and -averaging has enabled the correction of experimental scanning-distortions, reductions in electron beam-damage of samples, and improvements in signal-noise ratio (SNR) [3]. Very recently, a new ADF image analysis best-practice, melding the benefits of both reference-simulation and unbiased statistical interpretation based analysis methods, has produced an atom counting method with even greater robustness [4,5]. Exploiting these recent technical developments, we obtain optimised raw data which is fed into high-throughput image processing tools revealing particle size, atom-counts etc. Unfortunately, our increased analysis throughput merely shifts the investigation bottleneck from data-processing to interpretation. To remedy this, we have developed a computationally-efficient genetic-algorithm based structure solving code (requiring a few tens of CPU hours per structure on a standard desktop PC) to retrieve likely low-energy 3D particle structures which match the experimental observations.

Here we present results from a pure platinum nanoparticle sample supported on a 3D amorphous carbon used in the cathode of hydrogen fuel cells to aid the oxygen reduction reaction (ORR), Figure 2. Experimentally observed structures with fewer than 600 atoms were further used as inputs for full molecular dynamics (MD) and density functional theory (DFT) calculations using the DL_POLY4 and ONETEP codes respectively. These calculations reveal the effect of surface atomic-roughness on the local electronic density, the Smoluchowski effect (Figure 3). These results predict that adatoms present strongly over-binding sites and would lead to a form of “topographic-poisoning”. Using these DFT calculations we can predict the oxygen binding energy of various surface sites as a function of coordination-number, or particle size or crystallographic facet for example, and even to speculate about the chemical activity of members of the experimental ensemble.

A striking conclusion from this work is the need to shift our focus from obtaining and analysing singular beautiful images, to the collective analysis of large numbers of low SNR images from ensembles of particles; then to use these data to explore cohorts of likely candidate structures. Efforts are now underway to generalise this new approach to larger particles, different structures and to whole ensemble measurements (Figure 4); at which point comparative chemical activity studies could be pursued. [6]

References:

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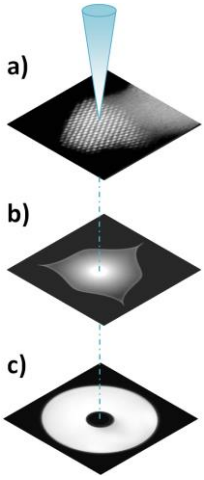

Figure 1. Examples of: a) an ADF image, b) a flux-map, and c) the detector sensitivity calibration.

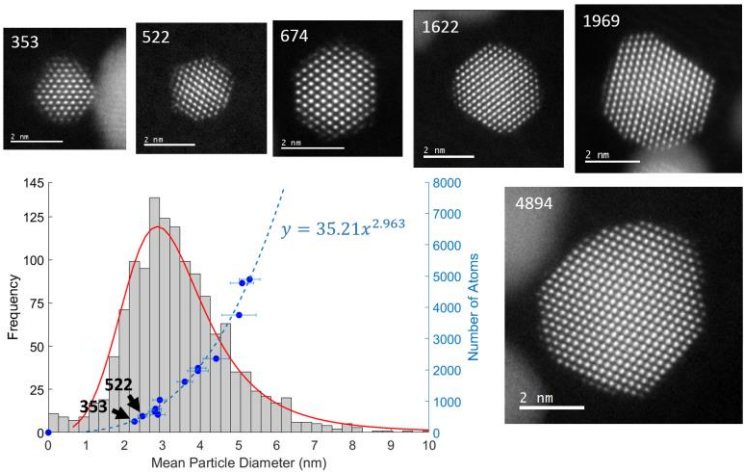

Figure 2. Contextualisation of the individual atom-counted images, atom counts inset, with respect to the wider size histogram (grey bars, left-axis). Individual particle masses follow a cubic relationship with diameter as expected (blue points, right-axis).

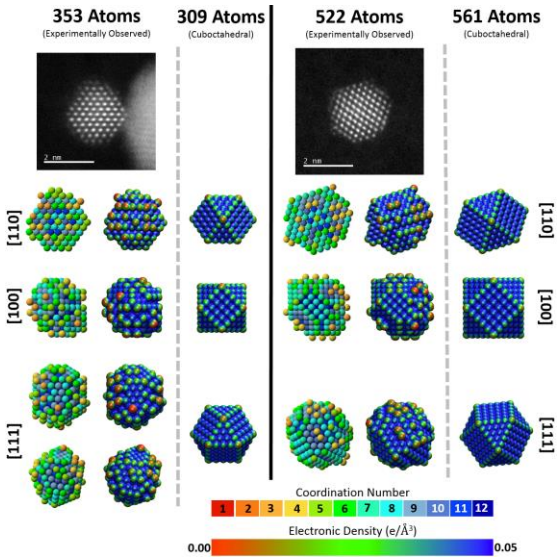

Figure 3. Visualising experimental 3D structural models coloured by coordination number and by electronic density (from DFT) reveals key features.

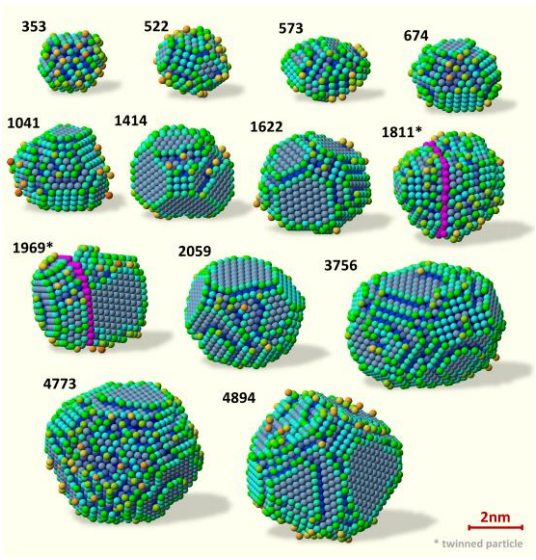

Figure 4. 3D models from across the whole size range studied, including rough, faceted, and twinned particles.

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