

## Simulating iDPC tomography of CeO<sub>2</sub> nanoparticles with experimentally realistic parameters and conditions

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Background incl. aims

Electron Tomography (ET) is a 3D analysis technique that produces a 3D reconstruction from a tilt series of microscopy images at 1-5° increments. Electron tomography can be used to characterise the 3D structure of nanoparticles at atomic resolution from an input of 40-150 images, depending on the specific reconstruction algorithm and parameters. Atomic electron tomography has been possible with HAADF-STEM for over a decade (Scott et al., 2012). However, a limitation of the technique is that prolonged exposure to the electron beam can cause damage or changes to samples, prohibiting an accurate reconstruction.

Integrated Differential Phase Contrast (iDPC) imaging is a technique which has contrast proportional to atomic electrostatic potential captured using a segmented detector. iDPC provides a better signal-to-noise ratio than HAADF at similar electron doses due to use of the bright-field disk and allows for atomic-resolution imaging with lower electron doses. iDPC additionally enables simultaneous imaging of light and heavy atoms, due to its image contrast being proportional to  $Z$  rather than  $Z^2$  as in HAADF (Lazić et al., 2016). Atom and defect positions at the surface of nanoparticles are crucial to catalytic performance. Accurate characterisation of 3D structure can therefore explain trends in catalytic activity/selectivity and assist in the rational design of catalysts. iDPC provides an excellent technique to image light atoms and their vacancies, even alongside atoms of higher atomic number. This is particularly valuable in the imaging of metal oxides, where surface termination and surface defect density can greatly impact catalytic properties.

We aim to demonstrate that an iDPC atomic resolution ET reconstruction is able to provide the locations of oxygen atoms, in addition to metal atoms within a nanoparticle. To investigate this, we simulate tilt series of iDPC and HAADF images, and generate tomographic reconstructions of a CeO<sub>2</sub> nanoparticle. CeO<sub>2</sub> was chosen due to its prevalence in catalysis and its requirement of a flux lower than  $7 \times 10^5 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$  to avoid beam damage (Johnston-Peck et al., 2016).

With these reconstructions, we assess the ability of iDPC tomography to distinguish between oxygen-terminated and cerium-terminated surfaces, and to detect surface oxygen vacancies. Additionally, we demonstrate that iDPC

will produce accurate tomographic reconstructions when applied at lower doses, resulting in reduced beam damage, compared to HAADF tomography.

### Method

Atomic models of octahedral ceria nanoparticles of lengths of 3 nm and 7 nm are built using the Python package Atomic Simulation Environment (ASE), using an additional Python package (Wulffpack) to adjust particle truncation based on surface energies.

iDPC-STEM and HAADF-STEM images of these models are simulated using the PRISM algorithm within the Python package abTEM (Madsen & Susi, 2020). We define set values of semiangle cutoff (17.5 mrad for iDPC, 30 mrad for HAADF), accelerating voltage (200 kV), PRISM interpolation factor (4) and collection angle (13-56 mrad for iDPC, 56-200 mrad for HAADF). A total of 151 images are simulated with tilt angles ranging from  $\pm 75^\circ$ . The effects of finite electron dose (via Poisson noise) and partial spatial coherence (via Gaussian noise) are added in post-processing.

3D reconstruction is performed using the ASTRA toolbox, applying the ASTRA-SIRT algorithm. TVM and GENFIRE reconstruction algorithms are also compared when using reduced numbers of projections. Reconstructions are formed with 1, 3 or 5° increments between each image. Determination of atom intensities in the resulting reconstructions are performed through ImageJ.

### Results

Oxygen atoms were clearly distinguishable in the tomographic reconstructions of the iDPC images (without the addition of noise). The SIRT iDPC reconstruction had a Ce:O intensity ratio of 170:60 compared to 135:5 for HAADF. The iDPC reconstruction additionally displayed a 177.6% intensity increase when comparing the locations of surface oxygens to vacancies, enabling clear differentiation between oxygen atoms and vacancies. This visible difference is demonstrated in the attached reconstruction slice graphic.

Partial spatial coherence (source size 0.2 – 0.4 eV), and finite electron doses ( $50 - 50000 \text{ e}^- / \text{\AA}^2$ ) were applied to successfully demonstrate the impact of these conditions on the quality of tomographic reconstructions. This has been quantified by measuring atom intensities in the reconstruction and assessed qualitatively by comparing the ability to visually distinguish individual oxygen atoms and vacancies without further processing. We plan to additionally assess aberrations (such as defocus). The SIRT iDPC reconstruction with a dose per image of  $5000 \text{ e}^- / \text{\AA}^2$  and a source size of 0.3 eV had a 256.50% intensity increase of the locations of surface oxygens compared to vacancies, showing vacancy detection is still feasible under low-dose experimental

conditions. This reconstruction also displayed a Ce:O intensity ratio of 104:44, compared to 23:5 for a HAADF reconstruction under the same conditions. This HAADF reconstruction contained no visible oxygens, as expected.

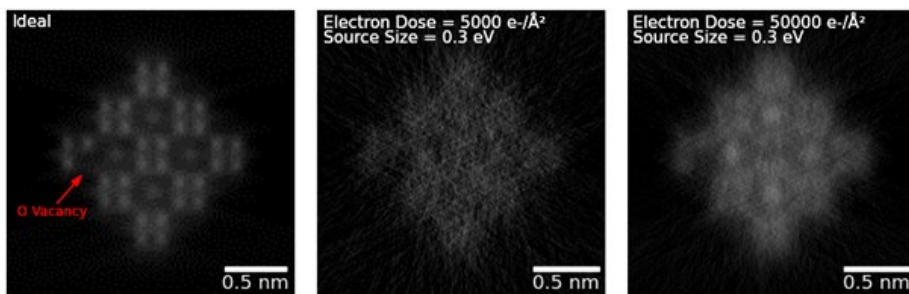
These simulations confirm the resolution limits of different acquisition conditions for iDPC tomography, enabling experimental application of optimum conditions, and a known error margin to operate within.

### Conclusions

Simulating iDPC and HAADF-STEM tomography has successfully confirmed parameters and requirements for atomic resolution iDPC tomography, enabling future experimental applications. By confirming the lower dose requirement for iDPC tomography, we have demonstrated the ability to create tomographic reconstructions of beam-sensitive samples which could not be captured with HAADF tomography.

We have additionally confirmed the ability of iDPC-STEM tomography to distinguish between vacancies and oxygen and cerium atoms within a 3D reconstruction of a CeO<sub>2</sub> nanoparticle. This demonstrates the potential of iDPC-STEM tomography as a technique for analysis of the surface termination of metal oxides, detection of oxygen vacancies and support-nanoparticle interface analysis.

### Graphic:



### Keywords:

Tomography, Python, iDPC, Simulation, Low-dose

### Reference:

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