Nanoparticles play an increasingly important role in catalysis. At the nanoscale, stoichiometry and the thermodynamic stability of different crystallographic facets may be modified as compared to the bulk, which is one of the reasons for their increased importance. Understanding activity and selectivity of nanoparticle catalysts requires detailed understanding of catalytic reactions at the atomic scale. An important step towards this goal is to obtain accurate atomic structures of catalytic nanoparticles and especially of their surface and immediate subsurface regions.

Aberration-corrected high resolution transmission electron microscopy (HRTEM) is a well suited tool for studying atomic structures of such particles. Quantitative analysis of the electron exit wave obtained from the experimental series of images with different focus can in principle provide some additional information on the three-dimensional structure.

In the present work we test an enhanced approach to quantitative exit wave restoration from the focal series of HRTEM images obtained for ceria nanoparticles. The existing linear exit wave restoration codes are based on the assumption that the sample under investigation is a weak-phase object. This approximation applied to a general object can result in an incorrect restoration. A more general approach is to reconstruct the exit wave by minimising the sum of squared differences between the simulated and experimental images where both the amplitude and the phase of the exit wave can be restored accurately. We suggest using the exit wave reconstructed by the linear approach as an initial approximation for this more general reconstruction. The successful restoration using the suggested method is dependent on knowing accurate aberration parameters of the microscope, especially the focus range and the focal step, and accurate image alignment in the experimental focal series. These are not routinely available from the actual experimental conditions. The suggested approach employs refinement of the exit wave together with both the aberration parameters and the image alignment in a single refinement cycle. The resulting exit wave is compared with exit wave obtained by theoretical multislice simulations and with the exit wave obtained by linear restoration software. We also investigate the origin of the increased contrast at the edges of the nanoparticles seen in the reconstructed phase, examining whether it is a consequence of adsorbed light species or a manifestation of electrostatic surface potential.

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Fig. 1: Global-refinement exit wave restoration algorithm implemented in the present study.

Fig. 2: Reconstructed electron exit wave amplitude a) and phase b) of ceria nanoparticles. Note the bright contrast at the edges of the nanoparticles in the phase image.