Quantitative Electron Ptychography of Sub-Stoichiometric Metal-Oxide Nanoparticle Catalysts Combined with HAADF-STEM Atom Counting

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In scanning transmission electron microscopy (STEM), local chemistry information of metal-oxide catalysts nanoparticles is obtained using spectroscopy. Electron Energy Loss Spectroscopy (EELS) is routinely used in combination with high-angle annular dark-field (HAADF) imaging to probe the local composition with nanometre resolution. However, to obtain a detectable signal, EELS requires high probe currents and long recording times, which, in small nanoparticles, may cause damage to the local stoichiometry. Here, we present an alternative method to obtain the local composition in oxide nanoparticles using quantitative electron ptychography on a direct electron detector. Because of their high recording speed and dynamic range, pixelated detectors allow recording ptychographic datasets with considerably lower currents and acquisition times than EELS, thus making a more efficient use of the electron dose. However, electron ptychography requires image quantification techniques to recover the local stoichiometry. Quantification methods that allow the counting of the number of atoms from image projections are well established for Z-contrast imaging modes, where the image counts increase monotonically with thickness [1, 2]. However, incoherent imaging techniques lack sensitivity towards light scattering elements meaning that HAADF atom counting is unsuitable for oxide nanoparticles. In contrast, electron ptychography detects all the scattering beams in 2D coherent electron diffraction patterns over a 2D image grid, from which the phase of the specimen exit wavefunction, containing both light and heavy elements, can be recovered [3]. This phase information is generally difficult to quantify due to coherence, however, because a ptychographic 4D STEM data set can be acquired simultaneously to a HAADF image, it is possible to calibrate the phase using atom counting. Here, we apply this novel quantitative ptychographic approach to determine the local sub-stoichiometric composition of CeO_{2-x} nanoparticles. Fig. 1 (a) illustrates a schematic of the 4D STEM ptychographic method, where the Ce atom count in (b), obtained from the simultaneously recorded HAADF image, is used to calibrate the ptychographic phase in (c) to count O atoms.

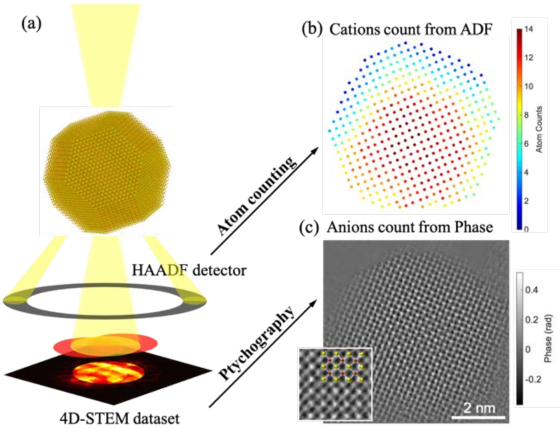

Figure 1. Schematic of quantitative electron ptychography applied to the measurement of local stoichiometry in ceria.

[1] L. Jones et al, *Nanolett.* **14** (2014) 6336.
[2] S. Van Aert et al, *Phys. Rev. B* **87** (2013) 064107.
[3] H. Yang et al, *Nat. Comm.* **7** (2016) 12532.