Supporting information

Identifying key structural features of IrO_x water splitting catalysts

*Elena Willinger[1,2], Cyriac Massué[1,2], Robert Schlögl[1,2] and Marc Georg Willinger[2,3]**

[1]*Max Planck Institute for Chemical Energy Conversion, Mülheim a.d. Ruhr, Germany*

[2]*Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

[3]*Max Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, 14424 Potsdam, Germany*

*e-mail: willinger@fhi-berlin.mpg.de

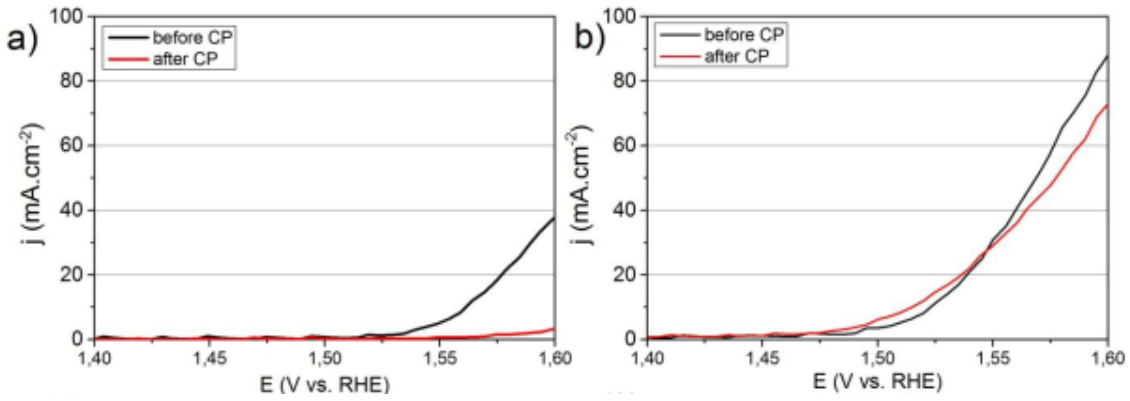

Figure S1. Linear sweep voltammetry measurements (5 mV.s-1) before (black line) and after the 2h-stability test (red line): a) IrO_x-commercial; b) IrO_x-FHI.[1] The stability test was performed using chronopotentiometry (CP) measurements at 10 mA/cm^2 for 2 hours.
While the IrO_x-FHI sample does not show change in OER activity, which is indicated by unchanged slope of LSV curves before and after stability test, the IrO_x-commercial sample show a significant decrease in OER-activity, refelected by a weaker LSV-slope. All details about electrochemical measurements can be found in the reference [1].

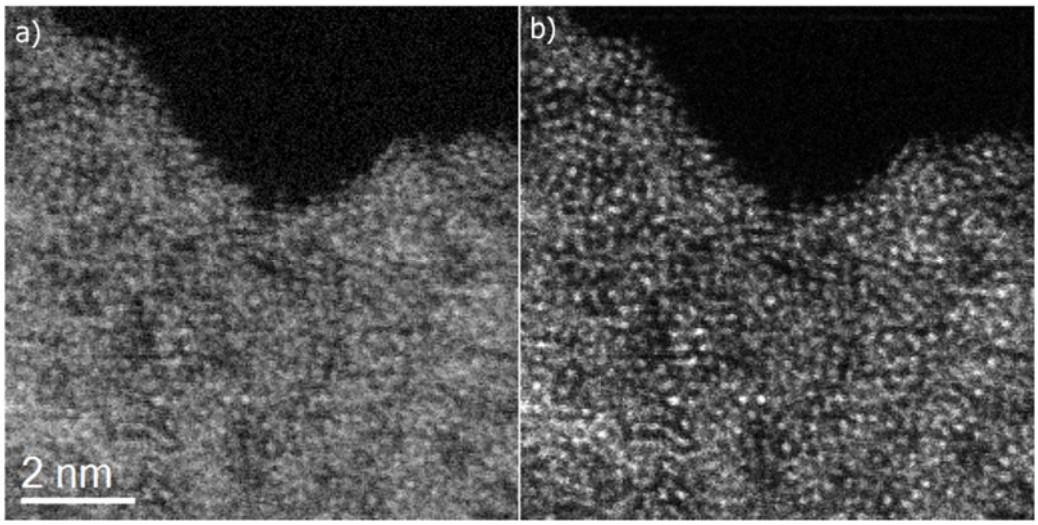

Figure S2. a) Original HAADF and Fourier filtered HAADF images of the IrO_x-FHI.

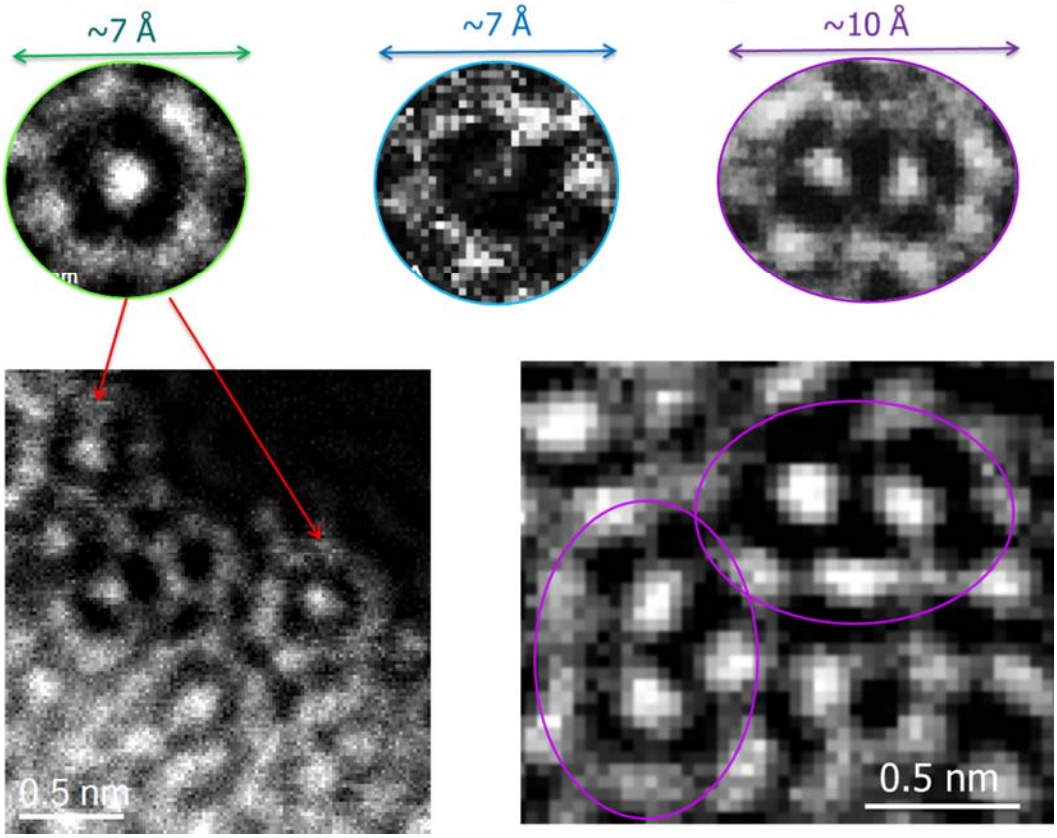

Figure S3. HAADF images of specific Ir clusters and their building blocks.

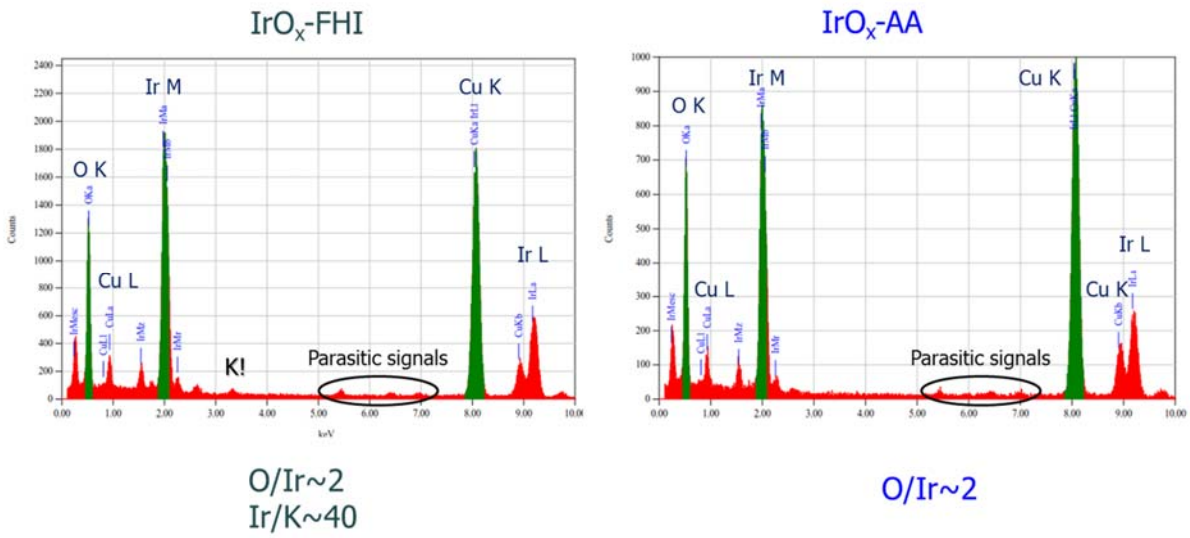

Figure S4. EDS analysis of elemental composition Ir hydroxides.

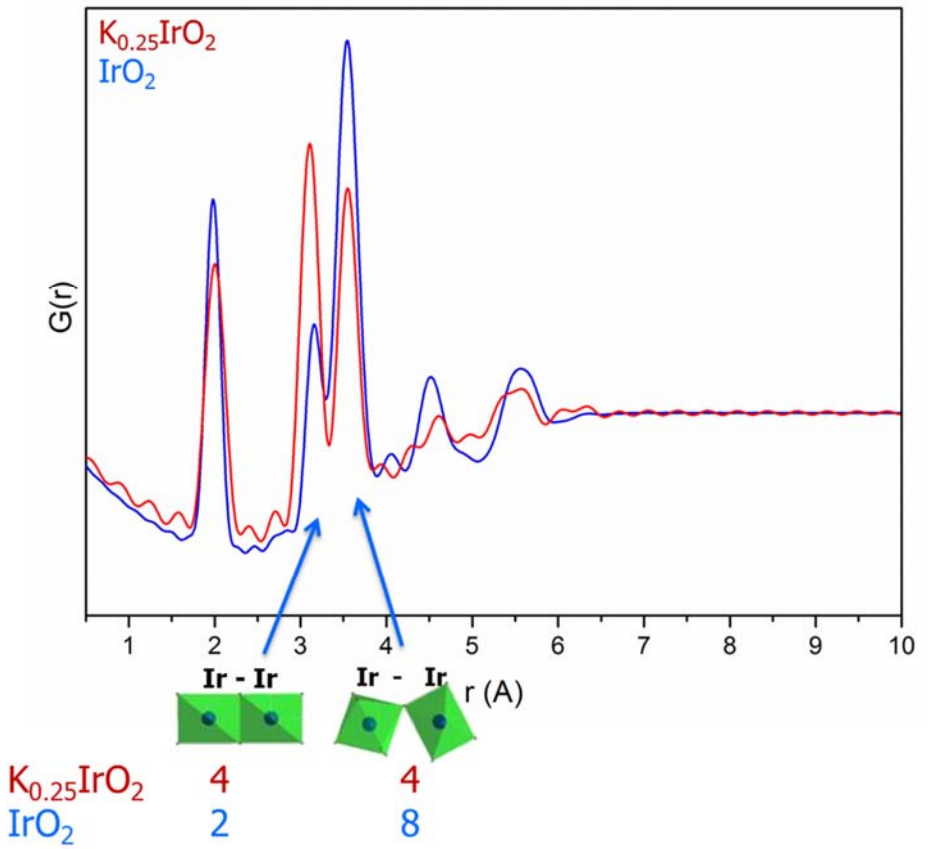

Figure S5. Calculated xPDFs of $K_{0.25}IrO_2$-hollandite and IrO_2-rutile for clusters of 7 Å sizes.

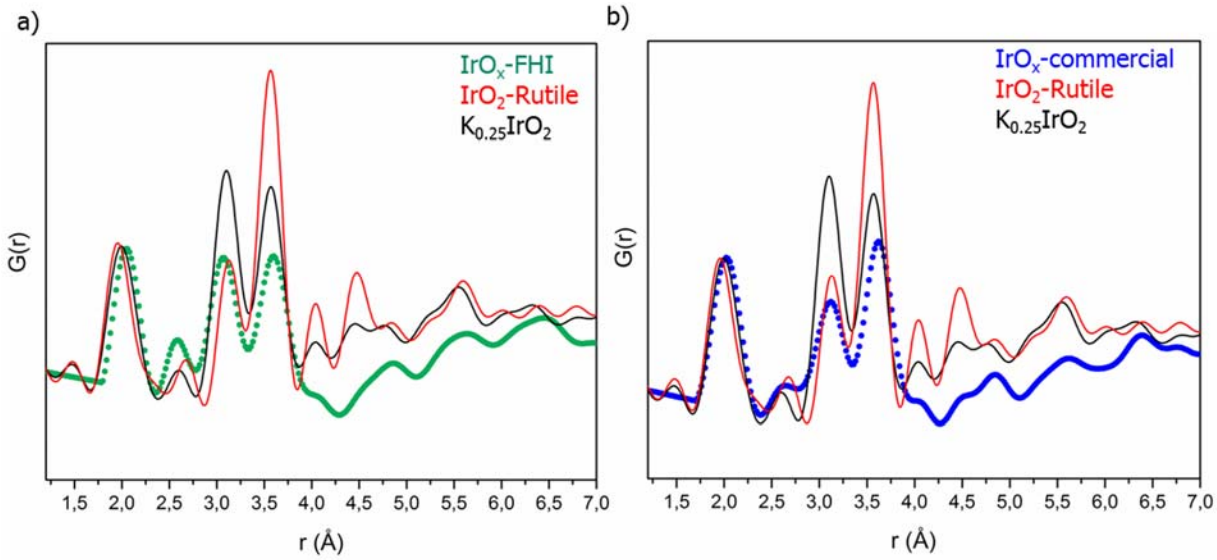

Figure S6. A comparison of the ePDFs of IrO_x hydroxides with the calculated xPDfs of the nanosized IrO_2-Rutile (red line) and the $K_{0.25}IrO_2$-hollandite (black line). a) IrO_x-FHI (green line); b) IrO_x-commercial (blue line).

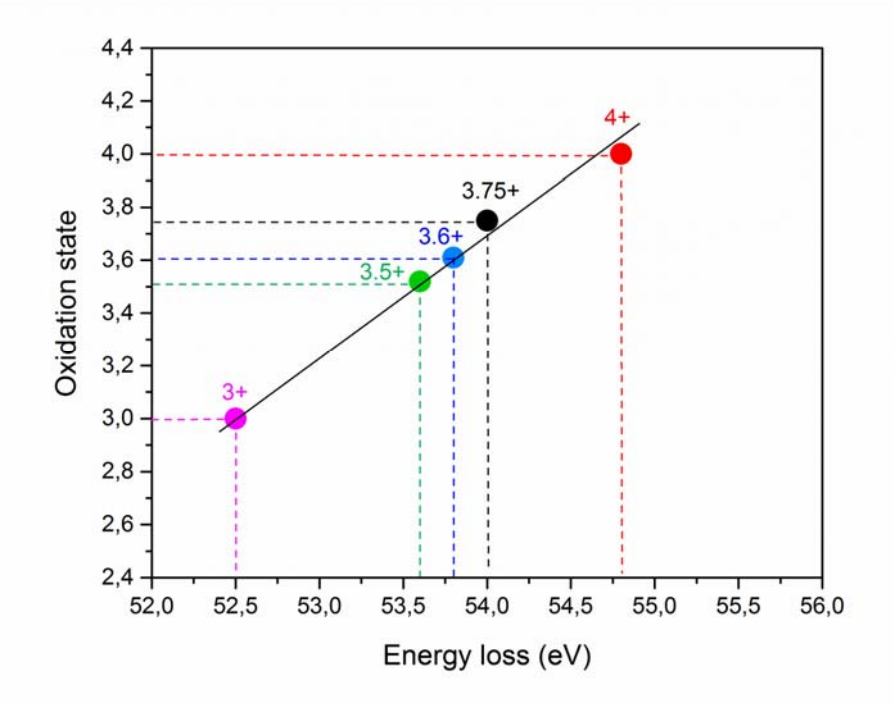

Figure S7. The plot shows the peak energy position of 2^{d}derevative of EELS Ir $O_{2,3}$-edge spectra as a function of Ir oxidation state ($IrCl_3$-magenda, IrO_x-FHI-green, IrO_x-commercial-blue, $K_{0.25}IrO_2$-black and IrO_2-red).

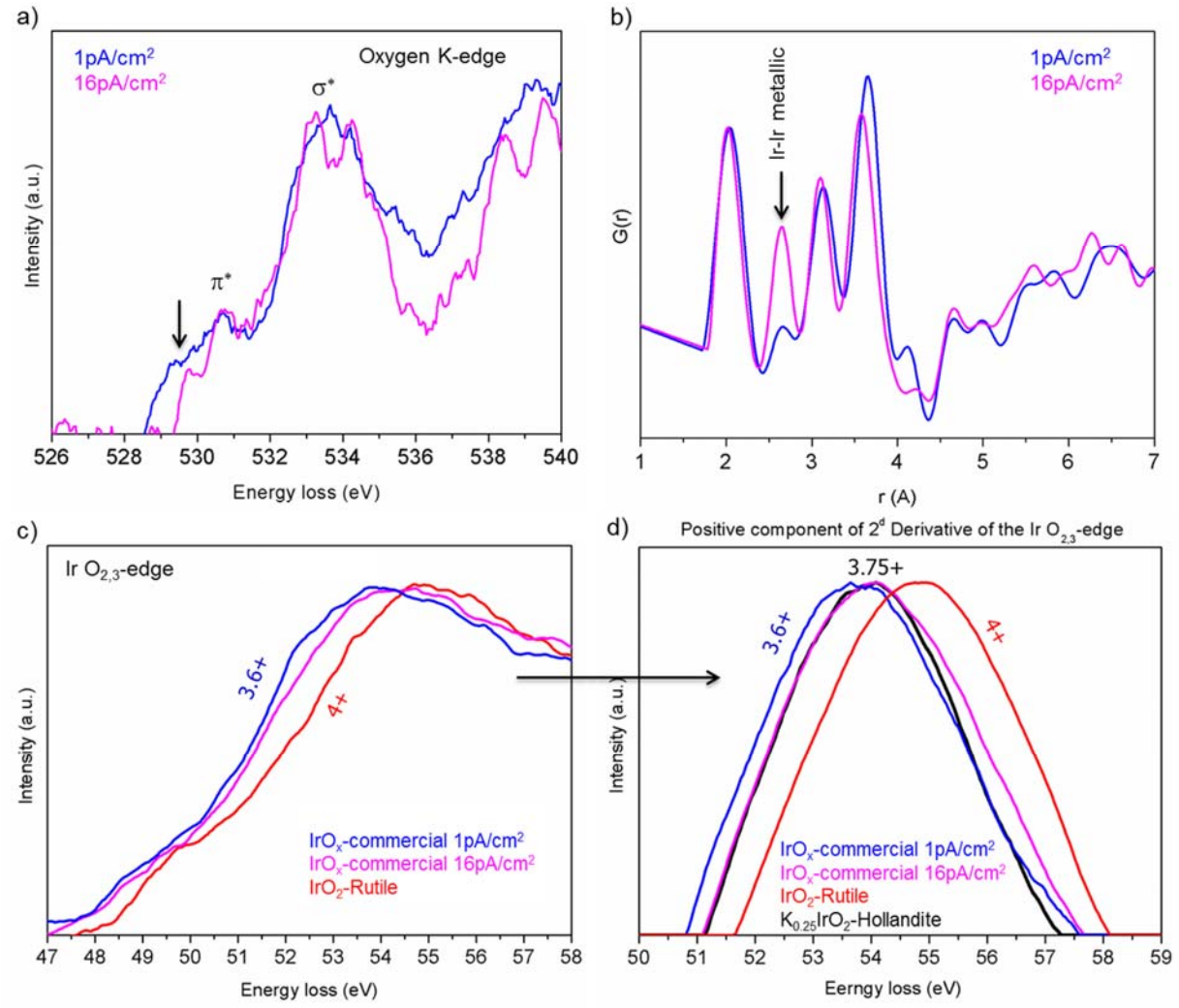

Figure S8. The electron beam intensity effect on the nano-and electronic structure of the IrO_x-commercial catalyst. All EELS spectra (diffraction mode) and corresponding diffraction patterns of shown ePDFs were measured under two different illumination conditions: 1pA/cm^2 (blue curve) and 16 pA/cm^2 (magenta curve) current density at 25 kx magnification. a) EELS Oxygen K-edge; b) ePDFs; c) A comparison of the EELS Ir $O_{2,3}$-edge of the IrO_x-commercial with the reference IrO_2 spectrum (red); d) A comparison of the positive component of 2^d Derivative of the Ir $O_{2,3}$-edge of the IrO_x-commercial with the reference IrO_2 (red) and $K_{0.25}IrO_2$ (black) spectra.

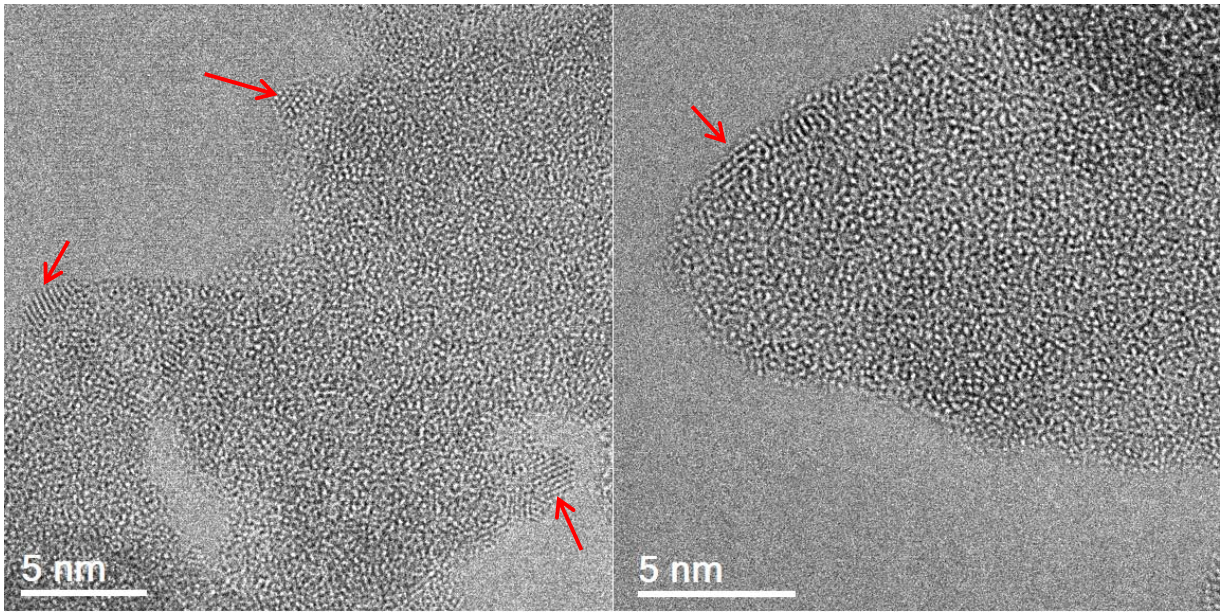

Figure S9. HRTEM images of IrO_x hydroxides showing formaiton of the Ir metallic phase (marked with red arrows) on the particle surfaces induced by e-beam irradiation.

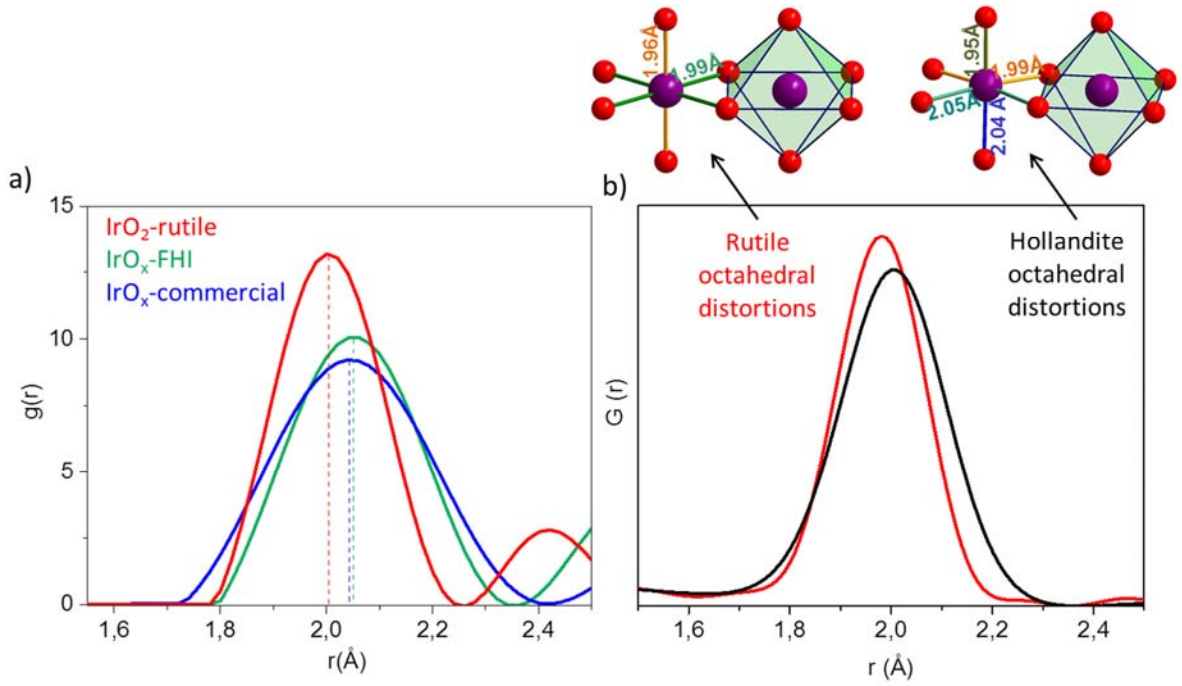

Figure S10. a) ePDFs of the first Ir-O pair correlation distances for the IrO_2-rutile sample (red), IrO_x -FHI (green) and IrO_x-commercial (blue); calculated xPDFs of the first Ir-O pair correlation distances for the $K_{0.25}IrO_2$ – hollandite (black) and IrO_2 – rutile (red). The octahedron models for the rutile and the hollandite structure clearly shows the difference of IrO_6 octahedral distrotions between these two structures.

References

1. Massué, C. Iridium oxohydroxide electrocatalysts for the oxygen evolution reaction, PhD thesis, Technical University of Berlin, Berlin, 09 May 2016.