### **Supporting Information**

## Ir nanoparticles with ultrahigh dispersion as oxygen evolution reaction

# (OER) catalyst: synthesis and activity benchmarking

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#### Colloidal dispersion



Figure S1. Iridium NPs dispersions in methanol at a concentration of 853  $\mu g_{lr} mL^{-1}$ . Picture (a) shows the fresh solution of IrCl<sub>3</sub> in methanol at a concentration of 20 mM. Picture (b) shows the colloidal NP dispersion after the synthesis, (c) 1-week old Ir NP dispersion after centrifugation at 5000 rpm for 10 min, and (d) 5-months old dispersion stored at room temperature. No sonication was performed to improve dispersion.

#### ECSA determination



Figure S2. CO stripping voltammetry profiles of the Ir NP with three different loadings at 20 mV s<sup>-1</sup> in 0.1 M HClO<sub>4</sub>. The CO adsorption process was carried out under potential control at 150 mV<sub>RHE</sub> for 120 s.

We determined the electrochemical active surface area (ECSA) by performing CO stripping measurements as described in the experimental section of the manuscript. The area under the CO stripping peak was integrated after background subtraction with a straight line between the onset

and the tail of the peak. This is different to the established method for Pt-based catalysts where the second scan typically is used for the background correction to consider the current associated to the oxidation of the metal. Such a procedure is feasible for Pt because the CO adsorption and oxidation is a reversible process after which the surface state is recovered. This is not the case for Ir for which the process is associated with an irreversible change in the surface as we demonstrated in this work. Consequently, the oxidative current in the potential range  $0.8 - 1.4 V_{RHE}$ , is higher for the first scan while it decreases during the subsequent CVs. The hysteresis is due to the stability of the iridium oxide which requires that the catalyst is not exposed at too high electrode potentials prior to CO adsorption. Therefore, in the first stages of the ECSA determination we did not scan the electrode potential above  $0.3 V_{RHE}$ .





Figure S3. Pictures of the Ir NP films with different coverages on the GC disks of the RDE tips taken with optical microscope. During the drying process, the RDE tips were rotated at 500 rpm in air to obtain a uniform thin film.

The qualitive morphology of the Ir NP films was investigated by optical microscopy.

TEM micrographs of a commercial Ir black



Figure S4. TEM micrographs of the commercial Ir black dispersions at two magnifications.

In contrast to the Ir NPs obtained by the Co4Cat synthesis approach, the commercial Ir black dispersion is instable and difficult to disperse. During drying large agglomerates with size in the range of hundreds of nanometers form. This is demonstrated in Figure S4a. A closer look at the aggregates with a higher magnification (Figure S4b) allows to distinguish smaller particles in the aggregates with a diameter of about 4 nm. The poor dispersibility of the Ir NPs likely accounts for the very low ECSA and MA reported in the manuscript.

Small angle X-ray diffraction (SAXS)



Figure S5. SAXS data (blue circles) of Ir NP suspension in methanol with the corresponding fit (black solid line) related to Figure 1a in the manuscript



#### X-ray Absorption Near Edge Spectroscopy

Figure S6. a)  $1^{st}$  derivative of the in-situ XANES spectra of Ir NPs recorded at different electrode potentials. The  $1^{st}$  derivatives were calculated after calibration of the edge position of the reference spectra of an Ir foil place after the sample (—). The normalized spectra are reported in the manuscript. The maximum of the  $1^{st}$  derivative has been used to determine the edge position. b)  $2^{nd}$  derivative of the in-situ XANES spectra of Ir NPs recorded at different electrode potentials. The energy at which the  $2^{nd}$  derivative crosses zero was used to determine the edge position. Datapoint density is 5 points/eV. In the table are reported the edge positions of different spectra as determined by a) and b).

## References materials for XAS



Figure S7. Normalized XAS spectra of Ir foil and  $IrO_2$  together with Ir NPs exposed to 0.1  $V_{RHE}$  and 1.5  $V_{RHE}$ .

Reproducibility of XAS spectra



Figure S8. Two XAS spectra consecutively recorded at 0.1  $V_{RHE}$  and at 1.5  $V_{RHE}$ .

We evaluated the reproducibility of the experiment by collecting two consecutive series of spectra on the same sample exposed to the very same potential. This was tested at the extremes of the potential range investigated, i.e. 0.1 and 1.5  $V_{RHE}$ . The curves reported in Figure S8 perfectly match indicating an extremely high reproducibility.

OER current contribution from GC substrate



Figure S9. Comparison of a linear potential scan of the bare glassy carbon electrode and one covered by Ir NPs. From  $1.2 - 1.55 V_{RHE}$  at 10 mV s<sup>-1</sup> in Ar saturated 0.1 M HClO<sub>4</sub>. Insert: Chronoamperometric potential step  $0.1 - 1.6 V_{RHE}$  in Ar saturated 0.1 M HClO<sub>4</sub>.

We tested contribution of the OER activity from the glassy carbon substrate by recording a potential scan from 1.2 to 1.55  $V_{RHE}$  as well as recording the chronoamperometric currents at a fixed potential of 1.6  $V_{RHE}$ . The comparison between the bare glassy carbon substrate with a glassy carbon electrode covered by Ir NPs confirms that contribution of the glassy carbon electrode is negligible.