

## Supplementary Information

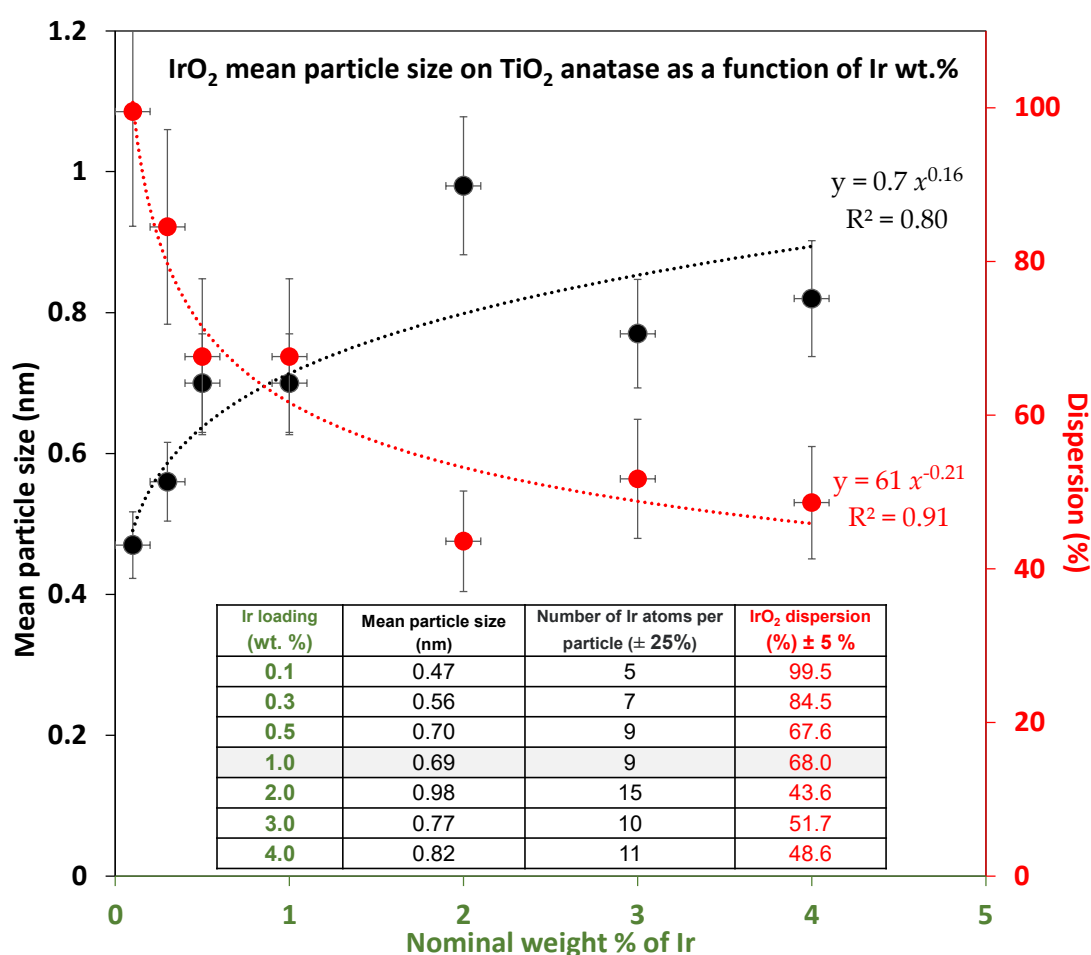


Figure S1

Relationship between the mean particle size and nominal weight % of IrO<sub>2</sub> on TiO<sub>2</sub> anatase. The dispersion is calculated from TEM measurements using the method described in the experimental section. Note the expected decay dependence of the dispersion as a function of increasing weight % (power decay function). The high % of errors in the number of Ir atoms per cluster is a reflection of the errors in mean particle size assuming that they reached an asymptote after 2wt.% of IrO<sub>2</sub>. The mean particle size was calculated by measuring the diameter of a minimum of 100 clusters.

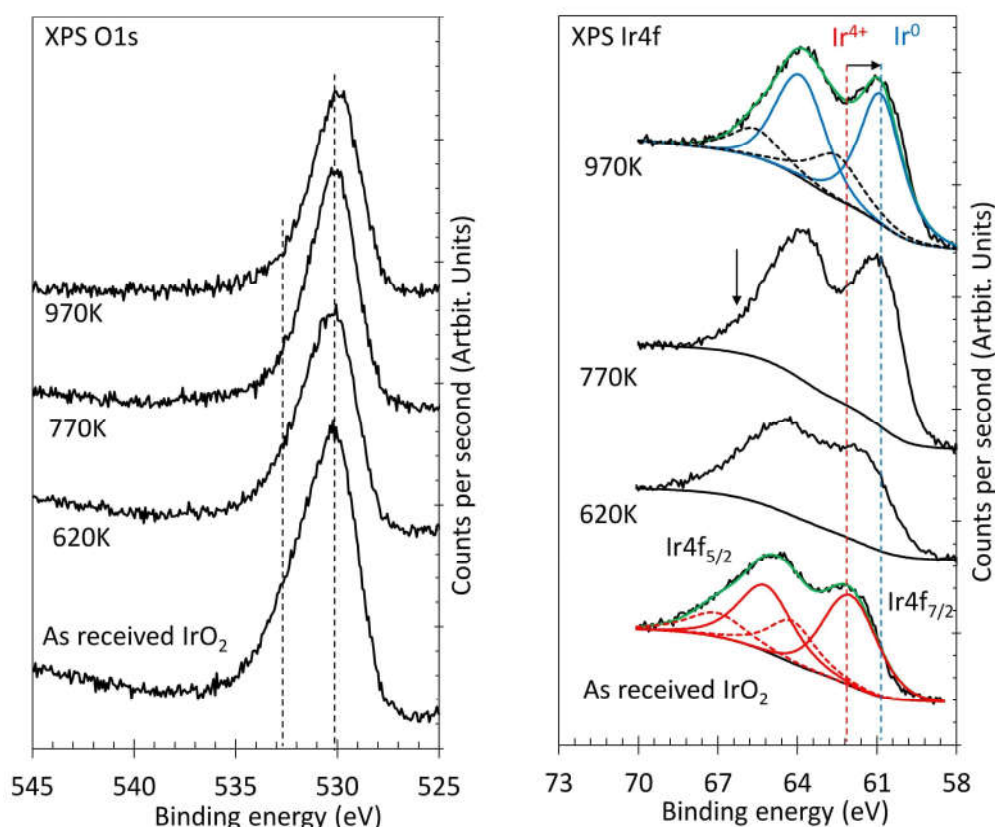


Figure S2.

XPS O1s and Ir4f of as received polycrystalline  $\text{IrO}_2$  as a function of heating inside the UHV chamber at the indicated temperature for 60 minutes, data are collected at room temperature. For the Ir4f of  $\text{IrO}_2$ , the solid lines are for  $\text{Ir}4f_{7/2,5/2}$  and the dashed lines are for their satellites while for the Ir4f of Ir metal the dashed lines are the remaining contributions of the signal which represent, in addition to satellites signatures of the remaining Ir cations that were not reduced. The temperature was measured at the holder (Ta plate) and therefore overestimated by up to 100K.

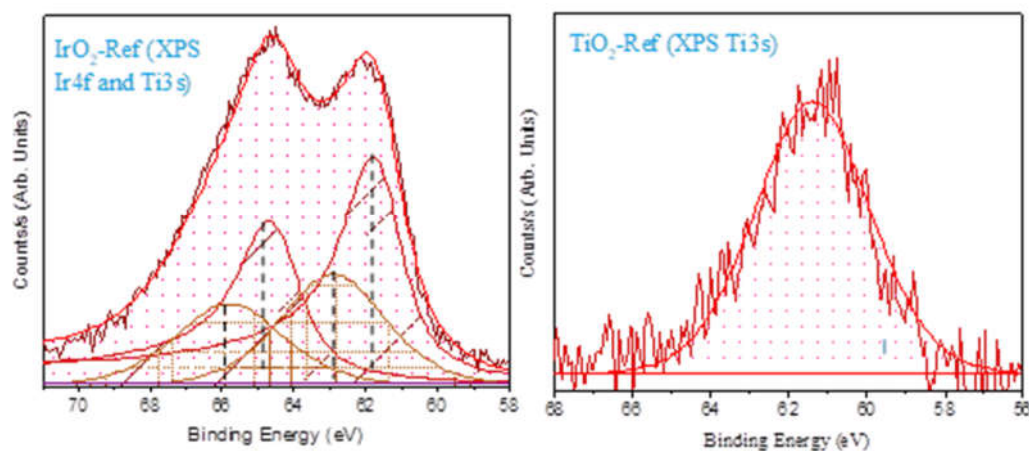


Figure S3.

*XPS spectrum of a) Ir 4f for IrO<sub>2</sub> rutile reference sample and b) Ti 3s for TiO<sub>2</sub> anatase reference sample.*

The Figure presents XPS Ir4f and Ti3s region for rutile IrO<sub>2</sub> (Sigma Aldrich) and TiO<sub>2</sub> anatase (Sigma Aldrich) reference sample. The peak fitting parameters including peak position, full width half maxima (FWHM), spin orbital splitting (SOS), peak area ratio and line shape were calibrated. Table S2 presents peak fitting parameters.

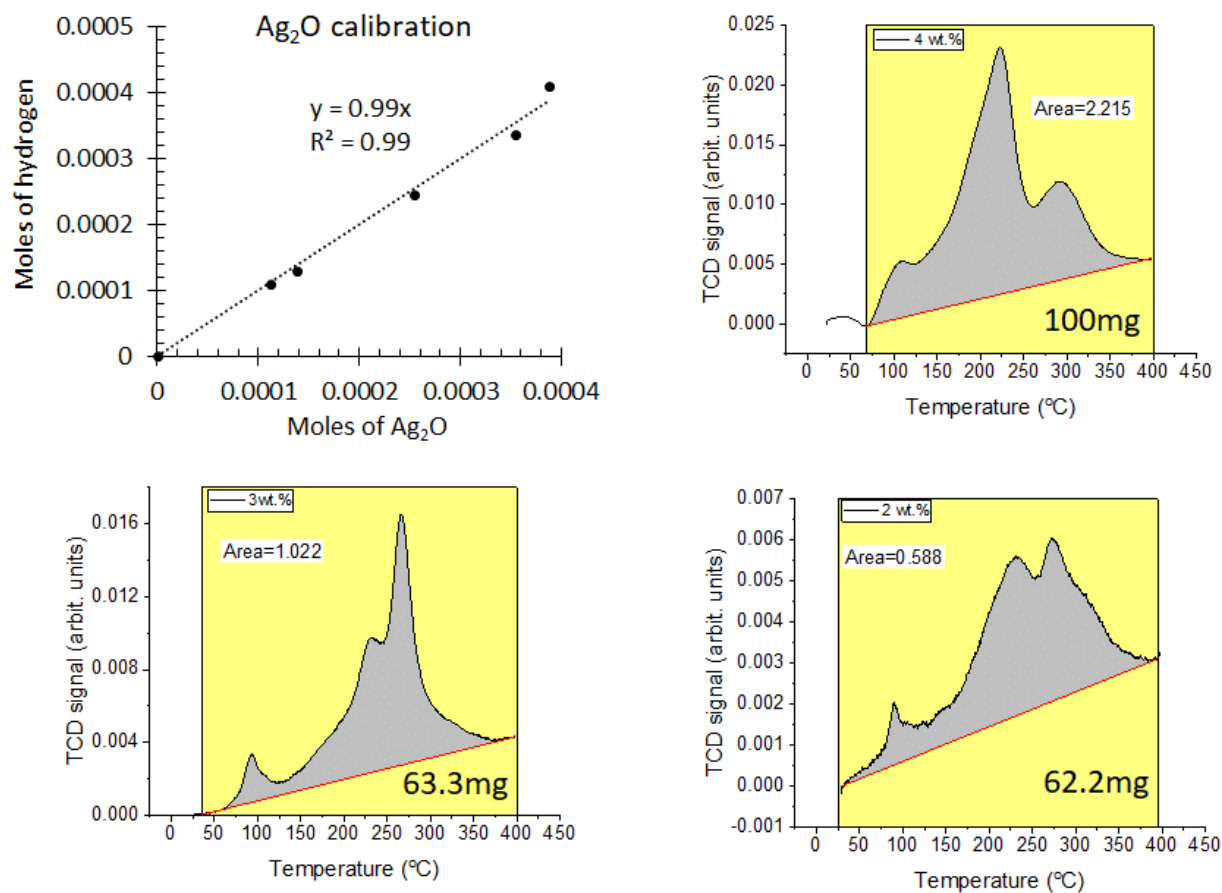


Figure S4

Top left figure:  $\text{Ag}_2\text{O}$  calibration line based on using samples of different weights ranging from 26 to 90 mg. The other figures are examples of peak area computation of Ir x wt.% on  $\text{TiO}_2$  from TPR results. The indicated areas are used to calculate the total hydrogen consumption from the calibration line.

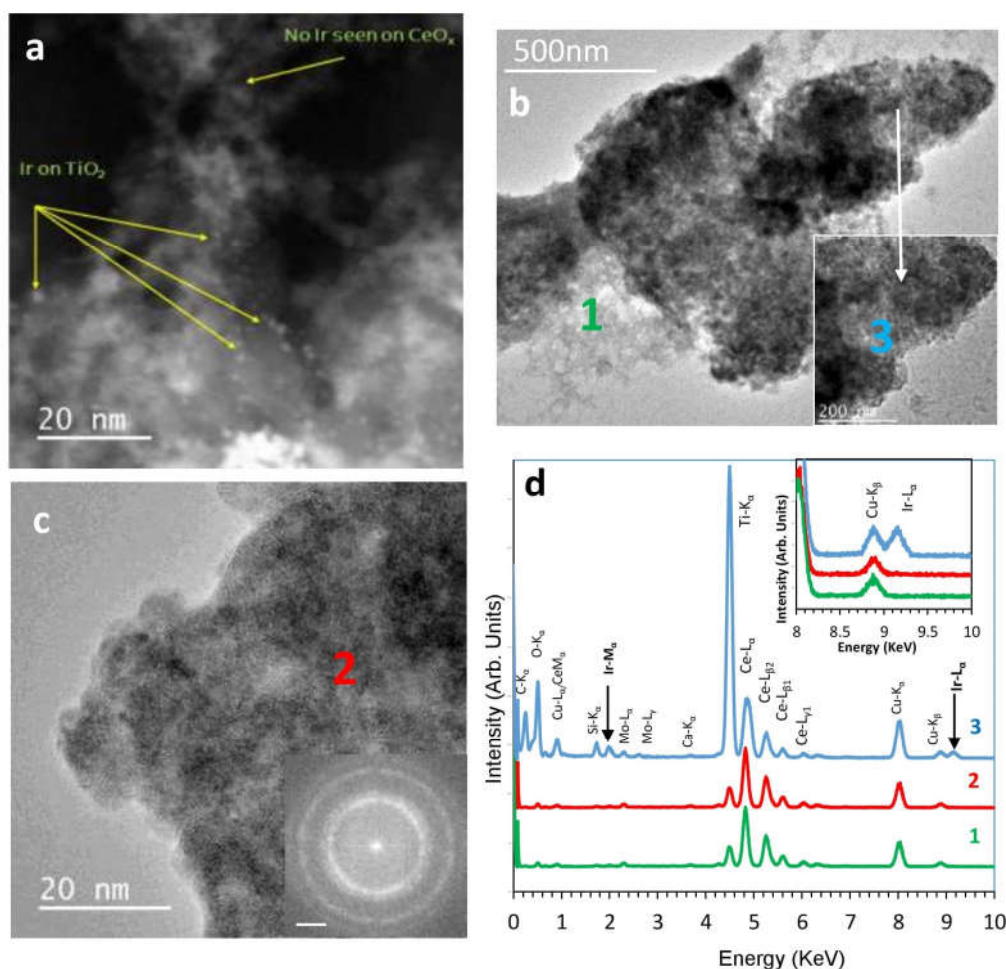


Figure S5.

4wt.% IrO<sub>2</sub>/TiO<sub>2</sub> spent catalysts after five successive runs with [Ce<sup>4+</sup>] cations = 0.182M. (a) STEM of the catalyst containing IrO<sub>2</sub>/TiO<sub>2</sub> (bottom) and CeO<sub>x</sub> (top). (b) TEM of a large area of the catalyst containing IrO<sub>2</sub>/TiO<sub>2</sub> and CeO<sub>2</sub> regions. Region 1 is mostly CeO<sub>x</sub> and the region 3 contains both TiO<sub>2</sub> and CeO<sub>x</sub>. (c) A pure CeO<sub>x</sub> area with the diffraction pattern of CeO<sub>2</sub>. (d) EDX of the areas labeled 1, 2, and 3 in (b) and (c); the inset is a magnifying area of the Ir<sub>Lα</sub> line position (Cu and Mo are from the sample mount).

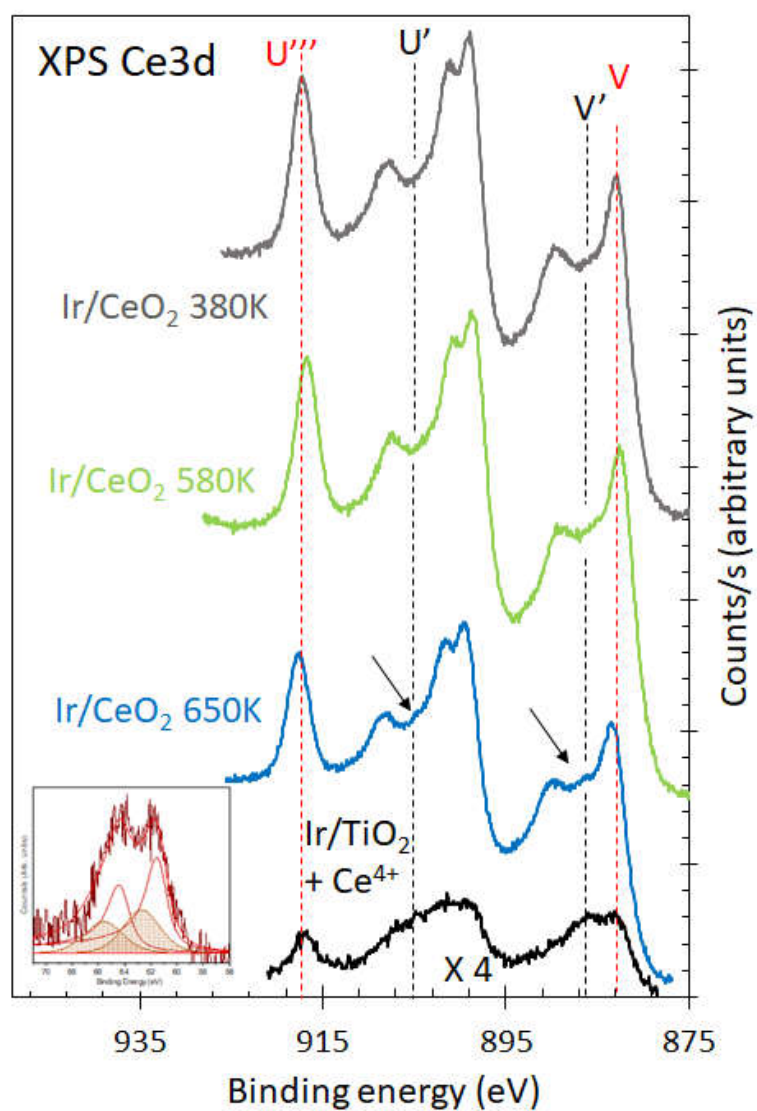


Figure S6.

XPS Ce3d of 1wt.% Ir/CeO<sub>2</sub> as a function of heating temperature inside the UHV chamber together with that of the spent IrO<sub>2</sub>/TiO<sub>2</sub> (the bottom spectrum x 4); the inset presents the Ir4f lines of the spent catalyst; TEM analysis indicated that Ir is deposited on TiO<sub>2</sub> and not on CeO<sub>2</sub> in the spent catalyst.

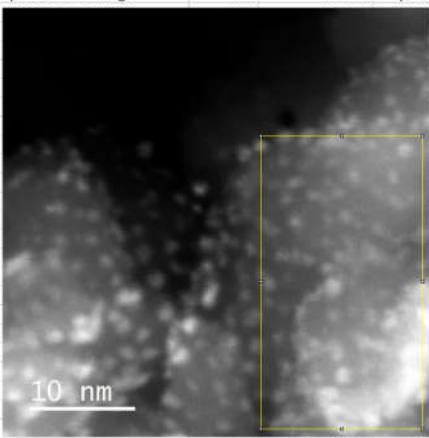
4 wt % loading			From STEM Image			
Ir wt. % loading	0.04 g		Total area of image	424,401 nm <sup>2</sup>	4.24401E-16 m <sup>2</sup>	
Ir at. Weight	192.217 g mol <sup>-1</sup>					
IrO <sub>2</sub> mol. Wt	224.22 g mol <sup>-1</sup>		No of IrO <sub>2</sub> partides in the image	128	4.16E-16	per 4.16E-16 m <sup>2</sup>
IrO <sub>2</sub> wt. % loading	0.046659765 g					1.0048E-16 2D
IrO <sub>2</sub> particle radius	0.5 nm	5E-10 m				0.236757218 coverage
IrO <sub>2</sub> density	11.66 g cm <sup>-3</sup>					
IrO <sub>2</sub> partide volume	2.94375E-28 cm <sup>3</sup>					
IrO <sub>2</sub> partide mass	3.43241E-27 g					
No of IrO <sub>2</sub> partides per g of catalys	1.35939E+25 number					
particle area (3D)	1.57E-18 m <sup>2</sup>					
particle area (2D)	7.85E-19 m <sup>2</sup>					
size of TiO <sub>2</sub>	25 nm					
area of a particle	1.9625E-15 m <sup>2</sup>					
volume of a particle	8.17708E-24 m <sup>3</sup>					
area of a particle covered by IrO <sub>2</sub>	4.64636E-16 m <sup>2</sup>					
density of TiO <sub>2</sub>	4260 kg/m <sup>3</sup>					
weight of one particle	3.48344E-20 kg	3.483E-17 g				
number of particle in one g	2.87073E+16 number					
total area of one g	56.33802817 m <sup>2</sup>					
total area of IrO <sub>2</sub> in one g	13.33843481 m <sup>2</sup>					
total number of IrO <sub>2</sub> in one g	5.33537E+19 number	2D				
total number of IrO <sub>2</sub> in one g	1.06707E+20 number	3D				
total number of IrO <sub>2</sub> in 20 mg	1.06707E+18 number	2D				
total number of IrO <sub>2</sub> in 20 mg	2.13415E+18 number	3D				

Figure S7.

Example (4 wt. % Ir/TiO<sub>2</sub>) for the calculation of the number of Ir atoms in IrO<sub>2</sub> clusters covering the surface of TiO<sub>2</sub> anatase from STEM assuming a hemispherical shape of IrO<sub>2</sub> clusters. The number is used to extract the Turn over number for the reaction.

**Table S1.**

*A. Calculated corrected peak area, relative sensitivity factors (RSF), and atomic percentage for the as-prepared 4 wt.% IrO<sub>2</sub>/TiO<sub>2</sub>.*

Species	Area	RSF	Cor. Area	At%
Ir 4f	614.19	4.22	146	0.6
Ti 2p	9369.2	1.8	5211	21.5
O1s	13486	0.71	18967	77.9

*B. Calculated corrected peak area, relative sensitivity factors (RSF), and atomic percentage for the used (after five consecutive runs of about 500 minutes in total) with [CAN] = 0.18 M) 4 wt.% IrO<sub>2</sub>/TiO<sub>2</sub>*

Species	Area	RSF	Cor. Area	At%
Ir 4f	450.81	4.22	107	0.5
Ti 2p	8104.81	1.80	4508	22.1
Ce 3d	7194.19	7.4	972	4.8
O1s	10531.2	0.71	14812	72.6

**Table S2.**

*List of fitting constraints used for Ir 4f fitting components obtained from Ir4f, and Ti3s regions of IrO<sub>2</sub>, and anatase TiO<sub>2</sub> reference powders.*

Species	Ir <sup>(IV)</sup> <sub>7/2</sub>	Ir <sup>(IV)</sup> <sub>5/2</sub>	Ir <sup>(IV)</sup> <sub>7/2</sub> Sat.	Ir <sup>(IV)</sup> <sub>5/2</sub> Sat.	Ti 3s
Line Shape	Dorian Stretch DS (0.13, 140)	Dorian Stretch DS (0.13, 140)	Gaussian- Lorentzian (0)	Gaussian- Lorentzian (0)	Gaussian- Lorentzian (0)
Binding Energy (eV)	61.8	64.7	62.3	65.2	61.2
FWHM (eV)	1.9	2.0	2.5	2.6	2.8