Supporting Information for:

An Aqua Regia-Free Chemical Recovery and Reprecipitation of Ir from IrO_x Catalysts: Optimisation of the Extraction Efficiency using Surface Response Methodology

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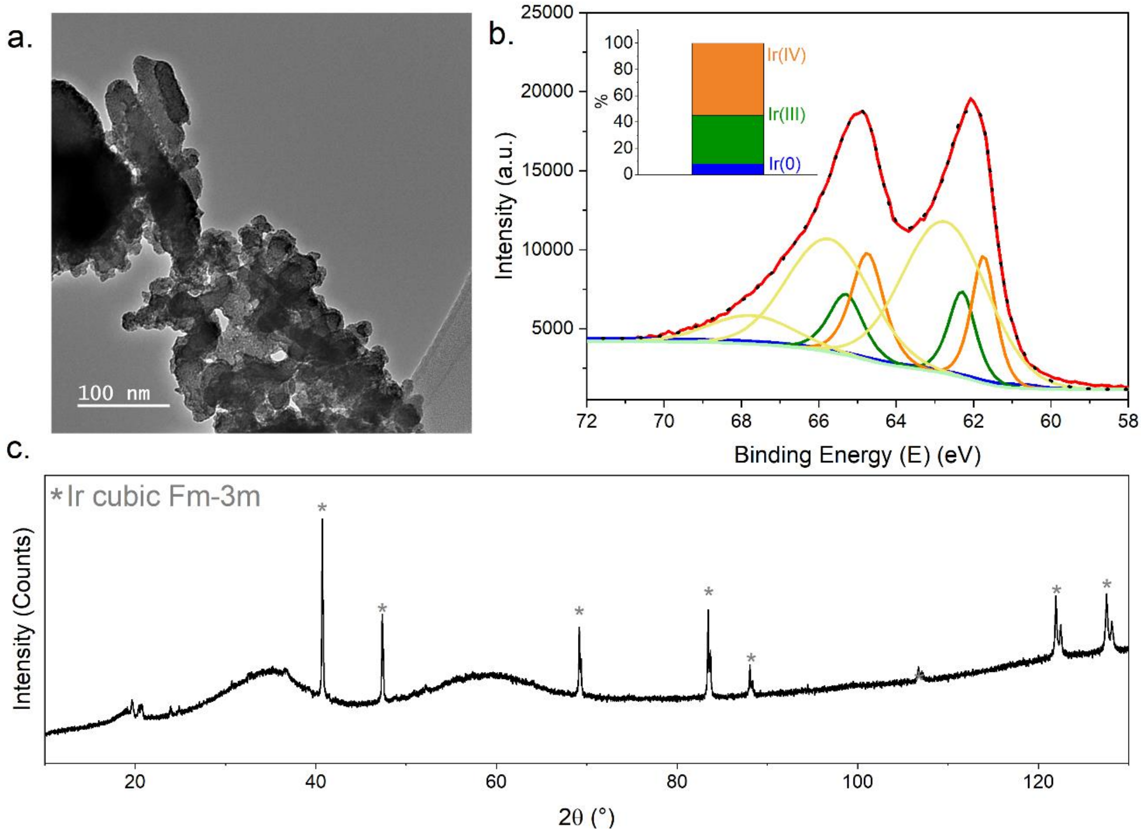

Figure S1 – a) TEM images, magnified 50k times, of $IrO_2.2H_2O$ from Thermo Scientific. b) X-ray photoelectron spectra (Ir 4f band) of the commercial $IrO_2.2H_2O$ catalyst. The black dots correspond to the measured spectra, the red line to the fitted spectra. The contributions of Ir(0), Ir(III) and Ir(IV) are described by the blue, green and orange lines, respectively. The yellow and cyan lines correspond to the contribution of the Ir(IV) and Ir(III) satellites respectively. c) X-ray diffractograms obtained on $IrO_2.2H_2O$. The stars correspond to cubic Fm-3m Ir phase (PDF card 00-006-0598).

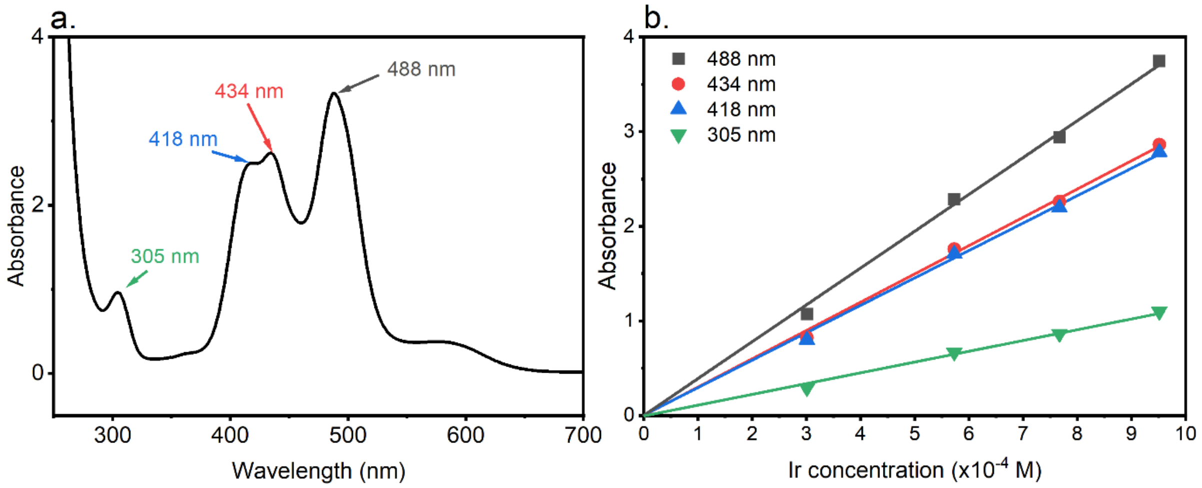

Figure S2 – a) UV-vis spectrum of $IrCl_6^{2-}$ species in HCl after microwave-assisted leaching of $IrO_2.2H_2O$. *T* = 200°C, hold *t* = 30 min, S/L = 0.25 g L^{-1}, 4 M HCl. The corresponding wavelength of the four peaks are given. b) Calibration curves of the absorbance against concentration of Ir in $H_2IrCl_6.xH_2O$ in standard solutions.

Table S1 - Masses of $H_2IrCl_6.xH_2O$ in 20 mL standard solutions, the concentrations of Ir and standard error from the imprecision in the balance are displayed

Mass of $H_2IrCl_6.xH_2O$ (mg)	**Ir concentration (ppm)**	**Ir concentration (x 10^{-4} M)**
3.1 ± 0.1	58 ± 2	3.0 ± 0.1
5.9 ± 0.1	110 ± 2	5.7 ± 0.1
7.9 ± 0.1	147 ± 2	7.7 ± 0.1
9.8 ± 0.1	183 ± 2	9.5 ± 0.1

Table S2 - Summary for the plot graph of Ir standard solutions.

Wavelength (nm)	**Slope (*εl*)**		**Statistics**
	Value	*Standard Error*	*Adj. R-Squared*
488	3897.7	0.005	0.999
434	2987.2	0.004	0.999
418	2903.2	0.004	0.999
305	1139.2	0.002	0.998

Table S3 - Selected factors and their range for the factorial design of the extraction of Ir in microwave conditions.

Factor	**Factor unit**	**Code**	**Level**	
			-1	1
S/L	g L^{-1}	A	0.1	0.25
[H^+]	M	B	0.5	4
[Cl^-]	M	C	0.5	4
Temperature	°C	D	70	200
[H_2O_2]	%v/v	E	0	3

Table S4 - Experimental screening Design of Experiments (DOE) and response in Ir extraction efficiency with chosen factors at given levels in microwave leaching conditions. Hold t = 30 min.

Run	**Factor**					**Response in Ir extraction efficiency (%)**	**Response in Ir mass extraction** $(\mathbf{mg_{Ir}\ g_{IrO_x}^{-1}})$
	A – S/L ($g\ L^{-1}$)	*B –* $[H^+]$ *(M)*	*C –* $[Cl^-]$ *(M)*	*D – Temperature (°C)*	*E –* $[H_2O_2]$ *(%v/v)*		
1	0.25	4	4	70	0	20	128
2	0.1	0.5	0.5	70	3	0	0
3	0.1	4	0.5	200	3	55	400
4	0.25	0.5	4	70	3	12	81
5	0.1	0.5	0.5	200	0	55	401
6	0.25	0.5	4	200	0	49	360
7	0.1	0.5	4	70	0	39	267
8	0.1	0.5	4	200	3	65	399
9	0.1	4	0.5	70	0	31	225
10	0.25	4	0.5	200	0	37	272
11	0.1	4	4	70	3	22	121
12	0.1	4	4	200	0	81	544
13	0.25	4	0.5	70	3	13	93
14	0.25	0.5	0.5	70	0	4	11
15	0.25	4	4	200	3	64	466
16	0.25	0.5	0.5	200	3	72	529

Table S5 - ANOVA statistical results for effects and interactions on the Ir dissolution efficiency obtained after model refining.

Source	Effect	Sum of Squares	Contribution (%)	*p*-value
Model		9221	100	<0.0001
S/L	Negative	355	4	0.0284
$[H^+]$	Positive	10	0.001	0.3755
$[Cl^-]$	Positive	453	5	0.0164
Temperature	Positive	7177	74	<0.0001
Interaction S/L and $[H_2O_2]$	Positive	815	8	0.0034
Interaction T and $[H_2O_2]$	Positive	411	4	0.0205

Table S6 – Obtained statistical factors of the screening analysis.

***p*-value**	> 0.1
Adjusted R squared	0.95
Predicted R squared	0.90
Coefficient of variation [%]	13.04

Table S7– Optimization and validation of Ir extraction model.

Analysis	Temperature (°C)	$[Cl^-]$ (M)	$[H_2O_2]$ (%v/v)	Predicted mean
Ir extraction efficiency (%)	139	1.6	3	91
Ir mass extraction ($mg_{Ir}\ g_{IrOx}^{-1}$)	139	1.6	3	769

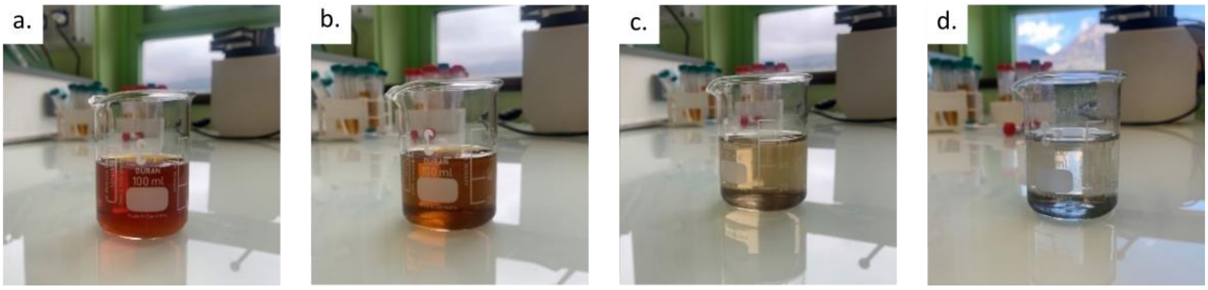

Figure S3 - Optical images taken during the precipitation reaction of $(NH_4)_2IrCl_6$ with addition of NH_4Cl to $IrCl_6^{2-}$ solution. The precipitate was left to crystallise for 72 h, and the pictures were taken after t = 0 h (a.), t = 24 h (b.), t = 48 h (c.) and t = 72 h (d.).

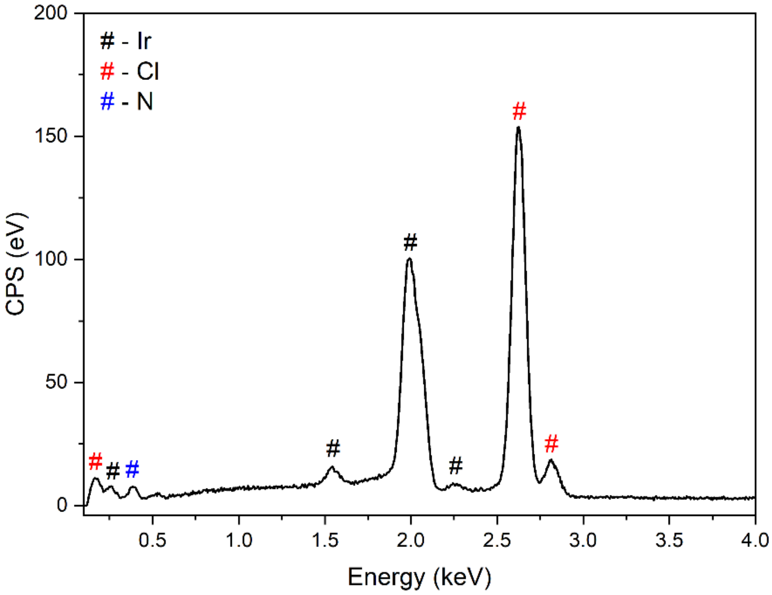

Figure S4 - Energy-dispersive X-ray spectrum of the $(NH_4)_2IrCl_6$ sample precipitate.

Experimental details

Microwave-assisted leaching

$IrO_2.2H_2O$ (99.99 %, Ir 73% min., Thermo Scientific Chemicals) was weighed on a balance of precision in a safety weighing enclosure dedicated for nanoparticles (a1-Safetech, ST1-150). The solid was transferred to modified polytetrafluoroethylene (PTFE) liners. Sulfuric acid (ACS reagent, CAS 7664-93-9, ≥ 97 %) was used to prepare solutions of desired concentration. Sodium chloride (ROTI®METIC, 99,999 %, 5N, CAS 7647-14-5) was used to prepare solutions of desired concentration as a chloride source. Hydrogen peroxide (Carl Roth® CAS 7722-84-1, 30 %) was used to prepare solutions of 5 % v/v concentration. Hydrogen peroxide of desired concentration was added dropwise to the leachate solution. Once loaded with the solid and leachate solution, the liners were closed with EasyPrep Plus vessel covers, sleeves and load disks, one per tube, and sealed in standard frame support modules (CEM). The reactions were conducted in a Mars 6™ (CEM) microwave reaction chamber. Experiments with leachates of different compositions were run separately according to the operating manual. The power was set at 400 W in the chamber and a temperature probe was inserted into one of the vessels. During the digestion time, the pressure inside the vessels was not recorded but allowed to increase up to 55 bar before degassing occurred. Microwave experiments were conducted at 70°C or 200°C with a ramp rate of 10 C min^{-1}. After reaction, the chamber of the Mars 6™ microwave oven was left to cool until reaching 50 °C before disassembling the vessels from the liners. The vessels were opened, carefully rinsed with MQ-grade water (Millipore, 18.2 MΩ cm, total organic compounds < 3 ppb), and transferred to tubes for analysis, taking note of the dilution. Products in which there was a low dissolution of Ir and remaining powder after reaction were transferred to centrifuge tubes and centrifuged for 15 min at 9000 rpm to facilitate the separation of the liquid and solid phases. Solutions were analysed by UV-vis spectroscopy on a Cary 4000 double-beam spectrometer to determine the concentration of Ir. A calibration of Ir concentration was performed using standard made from $H_2IrCl_6.xH_2O$ (Thermo Scientific Chemicals, CAS 16941-92-7, 99 % purity, Ir 38-42%) for UV-vis measurements. All UV-vis measurements were run against a blank of deionised H_2O. Stat-Ease 360® software was used for the Box-Behnken optimisation model.

Precipitation of leached IrO_2

NH_4Cl (Carl Roth®, CAS 12125-02-9, 99.7% purity) was added to the leachate solution at room temperature and the precipitate was left to crystallise for 72 h. The precipitate was filtered using a vacuum pump and analysed by X-ray diffraction θ-2θ mode on an X' Pert PRO MPD X-ray diffractometer using a Cu K_α radiation source (λ = 0.15419 nm) and energy-dispersive X-ray spectroscopy combined with scanning electron microscopy (SEM-EDS). The diffraction data was collected at a constant rate of 0.1° min^{-1} over an angle range of 2θ = 8-140°. SEM-EDS analysis was conducted on Zeiss Ultra 55 (Gemini® Technology).