Supporting Information

Green Synthesis of Water Splitting Electrocatalysts: IrO₂ Nanocages via Pearson's Chemistry

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Figure S1. (a) Scanning Electron Microscopy image and, (b) X-ray diffractograms of the initial Cu_2O particles and (c) of the particles recovered after CEP.



Figure S2. XPS spectrum in the Cu 2p region of the particles recovered after the CEP reaction. The data are plotted in orange, the fit of Cu(I) species in yellow, the fit of Cu(II) species in blue and the resulting overall fit in dashed line. Signal at 934.7 eV and 955 eV are attributed to $2p_{3/2}$ and $2p_{1/2}$ of Cu(II) in Cu(OH)₂.^[1] Corresponding satellites are found at 941 eV, 944 eV and 962.8 eV. The deconvolution of the main components allow to identify a small contribution of Cu(I) species at 932.4 eV and 952 eV and characteristics of $2p_{3/2}$ and $2p_{1/2}$ of Cu(I) in Cu₂O.



Figure S3. SEM images of the particles recovered after 20h of reaction in similar conditions that the synthesis of reference (a) but at (b) 30 °C and (c) 60 °C. While the morphology is well maintained at 20 °C, several IrO_2 particles precipitated besides the cubes can be clearly observed when the reaction is performed at 30 °C, and the morphology is even completely lost when the reaction is performed at 60 °C.



Figure S4: Modulus of the Fourier transform of the EXAFS signal of the deposited Ir-species (plain line) and corresponding fit (dashed line). The window used for the fit is in light blue. **Inset:** Scheme of the local Ir(III) environment in this species, the local geometry is hypothetical (Ir:blue, O: ref, CI: green, H: grey).

Sample	Shell	N	R/Å	σ² / Ų	$\Delta E_0 / eV$	R _f (%)	χ²red
Deposited Ir ^b	Ir-O	2.7	2.06	0.0033	9.9	2.23	35.10
		±1.4	\pm 0.04	± 0.0037	±0.2		
	Ir-Cl	4.0	2.35	0.0030			
		±1.2	\pm 0.01	\pm 0.0016			
Ir foil ^c	Ir-Ir ₁	12	2.71	0.0042	8.17	1.01	88.30
98-004-1524			\pm 0.001	\pm 0.0001	± 0.34		
(ICDD#)			(2.758)				
	lr-lr ₂	6	3.84	0.0056			
			\pm 0.006	\pm 0.0005			
			(3.900)				

Table S1: EXAFS fit Parameters for the deposited Ir species and the reference Ir foil^a

^a N, coordination numbers, r, distances between M (M= Ir or Cu) and neighboring atoms, σ , Debye Waller factors, ΔE_0 , scaling energy parameter and R_f goodness of fit. Bold numbers correspond to fixed values and uncertainties are given in italic. The reliability of the fit was assessed by the minimization of the reduced χ^2_{red} and metrics defined by the IXS standards and criteria committee (http://ixs.iit.edu/subcommittee_reports/sc/err-rep.pdf).

^b Those parameters were obtained by least square fitting over a 1.1-2.5 Å range of the Fourier transforms of the experimental EXAFS spectra (R-space, $k_{min} = 2.8 \text{ Å}^{-1}$ and $k_{max} = 10.6 \text{ Å}^{-1}$, Kaiser-Bessel window with dk = 1). ^c The fit of this sample was used to determine the value of the amplitude reduction factor $S_0^2 = 0.71$. Those parameters were obtained by least square fitting over a 1.0-4.0 Å range of the Fourier transforms of the experimental EXAFS spectra (R-space, kmin = 3.0 Å⁻¹ and kmax = 18.07 Å⁻¹, Kaiser-Bessel window with dk = 1). The mean distances determined from the crystallographic structure of Ir are reported for comparison purpose.



Figure S5. Cl/Ir ratio in the final cubes as a function of time of reaction obtained from SEM-EDX analysis (blue circles) and from EXAFS analysis (red triangle).

It can observed that the Cl/Ir ratio is almost constant in the particles which confirms that the chlorine in the final particle is only due to the presence of Ir chlorinated species and not to Cu species. The SEM-EDX experiment results show that the Cl/Ir ratio is of ca. 4, which is in agreement with the formula of the Ir species proposed in the final particles and determined from EXAFS spectra analysis: $Ir(OH)_2Cl_4$.



Figure S6. MCR-ALS analysis of the data set collected at the Ir L_3 edge during the reaction monitoring. Concerning the Iridium part, 3 components are needed to account for the evolution of the set of spectra and for explaining its variance. (LOF = 0.6%) (a) Log-scale representation of the scree plot obtained from

the PCA analysis of the L_3 -edge data set recorded during the replacement reaction. (b) Output file for the MCR-ALS minimization carried out for the Ir L₃ edge data set recorded during the reaction. This minimization has been carried out on a set of data including the normalized spectra of a 20 mM aqueous solution of $IrCl_3$ (blue component, spectrum index 1 to 5), the normalized spectra of the monitoring of the reaction (index 6 to 53) and the normalized spectra of the final deposited Ir-species (yellow component, index 54 to 60). So the evolution of the concentration profiles describes first the transformation of $IrCl_3$ into another soluble Ir-based species (red component, see Figure S6(c) and (d) for the modulus of the FT-EXAFS data), then an induction period before the Ir^{3+} ions start to precipitate in the $Ir(OH)_2CI_4$ form from the two soluble species. The second component might exist because the reaction media is not pure water but a 50 mM aqueous solution of NaCl. This component is an Ir³⁺ species with chlorine ions in the coordination sphere and is very similar to dissolved hydrated IrCl₃ in water. The sum of the concentration profiles of those two soluble IrCl₃-like species is reported Figure 3e and corresponds to the curve labelled Ir species in solution. (c) EXAFS spectra and (d) Fourier transformation of the EXAFS spectra isolated by MCR-ALS for the Ir evolution. The first component (green spectra) corresponds to IrCl₃ in aqueous solution, the third component (red spectra) is characteristic of the deposited Ir(III) species, identified as $Ir(OH)_2CI_4$, whereas the second component (blue spectra) displays characteristic features of Ir-Cl and an putative tiny contribution of Ir-O in its Fourier transform and seems very similar to IrCl₃ in solution.



Figure S7: **MCR-ALS analysis of the Cu part.** Output file for the MCR-ALS minimization carried out for the Cu K edge data set recorded during the replacement reaction. This minimization has been carried out on a set of data including the normalized spectra of a Cu₂O nanocubes dispersed in water (blue component, spectrum index 1 to 2), and the normalized spectra of the monitoring of the reaction (index 3 to 48). The procedure consisted in imposing the 3 components for the minimization and obtaining the corresponding concentration profile: in blue, the normalized spectra of a Cu₂O nanocubes dispersed in water (precursor material); in red, the normalized spectrum of a 20 mM aqueous solution of hydrated CuCl₂ (which dissociates in water to form Cu(H₂O)_x²⁺); in yellow, the normalized spectrum of the final particles obtained at the end of the reaction (recovered by centrifugation and dispersed in water with a 20 mM concentration based on a Cu₂O molar weight).



Figure S8. Modulus of the Fourier transform of the EXAFS signal of the deposited Cu-species (full line) and corresponding fit (dashed line). The window used for the fit is in light maroon. **Inset:** Scheme of the local Cu(II) environment in this species, the local geometry is hypothetical (Cu: orange, O:red).

Sample	Shell	N	R/Å	σ² / Ų	$\Delta E_0 / eV$	Rf (%)	χ²red
deposited Cu ^b	Cu-O	4.0	1.95	0.0058	10.7	0.87	519.70
		± 0.2	\pm 0.007	\pm 0.0010	±0.6		
	Cu-Cu	0.5	2.93	0.0061			
		± 0.5	\pm 0.03	\pm 0.0076			
Cu foil ^c	Cu-Cu ₁	12	2.55	0.0089	4.3	1.40	1333.59
98-004-3493			\pm 0.004	±0.0006	±0.6		
(ICDD#)			(2.556)				
	Cu-Cu ₂	6	3.58	0.0117			
			± 0.02	± 0.0019			
			(3.615)				
	Cu-Cu₃	24	4.46	0.0115			
			± 0.009	±0.0010			
			(4.427)				

Table S2: EXAFS fit Parameters for the deposited Cu species and the reference Cu foila

^a N, coordination numbers, r, distances between M (M= Ir or Cu) and neighboring atoms, σ , Debye Waller factors, ΔE_0 , scaling energy parameter and R_f goodness of fit. Bold numbers correspond to fixed values and uncertainties are given in italic.

^b Those parameters were obtained by least square fitting over a 1.0-3.0 Å range of the Fourier transforms of the experimental EXAFS spectra (R-space, $k_{min} = 3.0 \text{ Å}^{-1}$ and $k_{max} = 14.4 \text{ Å}^{-1}$, Hanning window with dk = 1).

^c The fit of this sample was used to determine the value of the amplitude reduction factor $S_0^2 = 0.91$. Those parameters were obtained by least square fitting over a 1.0-4.5 Å range of the Fourier transforms of the experimental EXAFS spectra (R-space, $k_{min} = 3.0$ Å⁻¹ and $k_{max} = 14.4$ Å⁻¹, Hanning window with dk = 1). The mean distances determined from the crystallographic structure of Cu are reported in brackets for comparison purpose.



Figure S9. (a) X-ray diffractograms of the materials obtained by CEP and calcined at 400, 450, 500 and 550 °C. IrO_2 reference (ICDD# 98-008-4577) is represented in red and CuO (ICDD# 98-062-8615) in black; (b) size of IrO_2 (red circles) and CuO (black square) crystallite size as a function of the calcination temperature.



Figure S10. TEM image of CuO-yolk/IrO₂-shell particles obtained after CEP and calcination at 550 °C. The particles have not yet been washed in acid, and the residual Cu-based core, crystallized into CuO upon calcination can be clearly observed in the center of the IrO_2 nanocage.



Figure S11. X-ray diffractogram of the particles after CEP and calcination at 550 °C (top) and further washed in acid (bottom). IrO_2 reference (ICDD# 98-008-4577) is represented in red and CuO (ICDD# 98-062-8615) in black. After acid leaching, the peaks characteristics of the CuO phase are not observed anymore. Only peaks characteristic of the IrO_2 rutile particles are observed.



Figure S12. (a) HRTEM image and (b) corresponding interplanar profile of a crystallite from the surface of the IrO₂ nanocages. The arrow indicates the direction of the profile.

[1] M. C. Biesinger, *Surface and Interface Analysis* 2017, *49*, 1325-1334.