Electronic Supplementary Information

Pt-Co₃O₄ Superstructures by One-Pot Reduction/Precipitation in Bicontinuous Microemulsion for Electrocatalytic Oxygen Evolution Reaction

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Material and Methods

PtOi-CoOi was synthesized dissolving Pt and Co organic precursors corresponding to 1 wt % of Pt and 1 wt % of Co in Isooctane. Thereafter, Synperonic[™]91/5, and Milli-Q water were added and vortexed to obtain 52% oil phase, 27.36% surfactant, and 20.64% water phase, and kept at 26 °C. At this temperature, the typical physical characteristics of BCME (transparent, fluid, and non-birefringent) were observed.

The synthesis of PtAq-CoOi was achieved by weighing the appropriate masses of Pt aqueous precursor and Co organic precursor to give 1 wt % of Pt in the final aqueous phase and 1 wt % of Co in the organic (isooctane) phase; these phases were mixed together with Synperonic[™] 91/5, to obtain 20.64 % water phase, 52 % oil phase and 27.36 % surfactant. The BCME was formed by vortexing, followed by keeping at a temperature of 19 °C.

For PtOi-CoAq, appropriate masses of Pt organic precursor and Co aqueous precursor were weighed and dissolved to give 1 wt % of Pt in isooctane and 1 wt % of Co in water. These phases were mixed with Synperonic[™] 91/5, to obtain 20.64 % water phase, 52 % oil phase and 27.36 % surfactant. The final mixture was kept at 25 °C.

Pt-HS was synthesized by dissolving an appropriate masses of Pt aqueous precursor to form 2 wt % of Pt in 20.64% Milli-Q water. 27.36 % Synperonic[™]91/5 and 52 % Isooctane were added to make the final mixture. The BCME was formed by vortex mixing for a few seconds and kept at 22 °C.

For each BCME containing the metallic precursors, NaBH₄ was used as the reducing agent. 100 µL of sodium borohydride solution with a concentration equivalent to twice the total sum of Co and Pt's moles was prepared and rapidly added under 3 seconds to the BCME, and vortexed during 5 seconds. Then the reaction mixture was kept unstirred at the corresponding temperature for microemulsion stability (PtOi-CoOi at 26 °C; PtAq-CoOi at 19 °C; PtOi-CoAq at 25 °C; Pt-HS at 22 °C) for 48 hours. The nanomaterials were isolated, washed and dried as described in the main manuscript.



Full Scale 1151 cts Cursor: 10.626 (5 cts) keV

Figure S1: EDS images of Pt-Co₃O₄(s): PtAq-CoAq (A), PtAq-CoOi (B), PtOi-CoAq (C), PtOi-CoOi (D), Pt HS



Figure S2. Schematic representation of the H₂ microbubbles evolved *in-situ* at the water channels, surrounded by surfactant molecules and dragging reducing species to the oil channels.



Figure S3: The XRD patterns of Pt-Co₃O₄-HSs: PtOi-CoOi (a), PtAq-CoOi (b), PtOi-CoAq (c).

Table S1. Table showing the peaks derive from the deconvolution of the Co $2p_{3/2}$ peak. The signals were assigned to Co³⁺ and Co²⁺ species with the corresponding satellite signals (shake-up).

Sample -	Binding energy (eV)			
	Co ³⁺	Co ²⁺	Co ³⁺ satellite	Co ²⁺ satellite
PtAq-CoAq	781.20	783.80	786.20	788.20
PtAq-CoOi	780.50	782.23	785.92	788.60
PtOi-CoAq	779.72	782.15	785.72	789.10
PtOi-CoOi	781.20	783.80	787.00	789.90