

**Supporting Information  
For**

**Exploring the Role of Polymer Interactions During Water Electrolysis  
under Basic Conditions with Bifunctional Cobalt Corroles**

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## **Materials and Methods**

### **General**

All chemicals and solvents (ACS or HPLC grade) were commercially available and used as received unless otherwise indicated. For all air-sensitive reactions HPLC-grade solvents were obtained as anhydrous and air-free from a PPT Glass Contour Solvent Purification System. UV-vis absorbance spectra were obtained on a Cary 60 from Agilent. Solid state UV-vis absorbance spectra were obtained on Perkin Elmer Lambda 850+ Diffuse Reflectance UV-vis spectrometer. The FEI Quanta 650 Field Emission Scanning Electron microscope was used to obtain the SEM-EDS data. Everhart-Thornley detector (ETD) is used to collect secondary electrons (SE). 15kV is the accelerating voltage, with a spot size ranging from 4.0-5.5 depending on the sample. The magnification is at 10,000x for all samples. High-Resolution Mass Spectra were obtained on an Agilent LC-QTOF. Transmission electron microscopy (TEM) images, providing insights into the metal distribution were obtained on a FEI Tecnai Spirit (120 kV). The contents of physisorbed Co species on the Vulcan Carbon were quantitatively assessed by using inductively coupled plasma optical emission spectrometry (ICP-OES) on a PerkinElmer Avio-200 ICP spectrometer. A Fastec IL5 camera with objective lens with pylon Viewer software was used for recording images and HAYEAR software was used for angle measurement.

### **Electrochemistry**

All electroanalytical experiments were performed using a Biologic VSP potentiostat. Aqueous mercury/mercury oxide (Hg/HgO) electrode was used as the reference electrode with 1 M KOH electrolyte. Glassy carbon and platinum wire were used as working electrode for HER and OER studies, respectively. Carbon paper coated with the catalyst ink (described below) was the working electrode. All the studies were carried out in 1 M KOH, bubbled with nitrogen. The ink was prepared by sonicating 1 mM or 3 mM concentrations of the metallocorrole with 12.5 mg of Vulcan carbon XC-72, 0.5 mL of 5% Nafion in 3.4 mL DCM and 1 mL of ethanol. All voltammograms were corrected for internal resistance and obtained at scan rates of 100 mV/s. All the potentials are referenced vs RHE.

### **General Synthesis of 2 and 3**

The preparation of 5,10,15-tris(pentafluorophenyl) corrole, **1R** and its Co(III) complex, **1** was carried out as previously reported.<sup>1,2</sup> 2R and 3R were synthesized, following the procedure similar to that previously reported for nucleophilic substitution reactions of **1R**<sup>3</sup>, by treating it with the desired primary amine (5 equiv) and heating it in DMSO at 100 °C for 5 h. Subsequently, the reaction mixture was poured into 200 mL of deionized water, before the crude aqueous suspension was extracted with ethyl acetate (4 x 100 mL) and purified by column chromatography over silica with 15% DCM in hexane as the eluent ( $R_f = 0.5$ ). **2** and **3** were synthesized following the same procedure as that of **1**, by stirring 5,10,15-Tris(4-heptylamino-2,3,5,6-tetrafluorophenyl)corrole, **2R**, or 5,10,15-Tris(4-dodecylamino-2,3,5,6-tetrafluorophenyl)corrole, **3R**, with NaOAc (15 equiv), Co(OAc)<sub>2</sub>•4H<sub>2</sub>O (6 equiv) and PPh<sub>3</sub> (8 equiv) in ethanol for 4 h followed by purification by column chromatography over silica with 20% of DCM in hexane as the eluent, followed by recrystallization from MeOH/pentane.

**1** was obtained in 73% yield (56 mg; 50.2 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ in ppm): 8.70 (d, <sup>3</sup>J<sub>H-H</sub> = 4.4 Hz, 2H; β-pyrrole H), 8.34 (d, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 2H; β-pyrrole H), 8.25 (d, <sup>3</sup>J<sub>H-H</sub> = 5.0 Hz, 2H; β-pyrrole H), 8.09 (d, <sup>3</sup>J<sub>H-H</sub> = 4.8 Hz, 2H; β-pyrrole H), 7.01 (t, <sup>2</sup>J<sub>H-H</sub> = 7.4 Hz, 3H; *para*-H of PPh<sub>3</sub>), 6.66 (m, 6H; *meta*-H of PPh<sub>3</sub>), 4.59 (m, 6H; *ortho*-H of PPh<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 470 MHz): -136.80 (dd, *J* = 24.3 Hz, *ortho*-F), -137.12 (dd, *J* = 24.1 Hz, *ortho*-F), -138.11 (dd, *J* = 21.8 Hz, *ortho*-F), -138.44 (dd, *J* = 25.3 Hz, *ortho*-F), -153.75 (dd, *J* = 23.8 Hz, *para*-F), -161.82 (m, *meta*-F), -162.23 (m, *meta*-F), -162.43 (m, *meta*-F). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 202 MHz): 26.73. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ in nm (ε in M<sup>-1</sup>cm<sup>-1</sup>): 376 (46000), 410 (48500), 551 (9380), 585 (9380); MS: *m/z*: C<sub>55</sub>H<sub>23</sub>CoF<sub>15</sub>N<sub>4</sub>P; [M+H]<sup>+</sup>: 1114.0752; obtained: 1114.0735.

**2** was obtained in 73% yield (32 mg; 23 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ in ppm): 8.57 (d, <sup>3</sup>J<sub>H-H</sub> = 4.3 Hz, 2H; β-pyrrole H), 8.32 (d, <sup>3</sup>J<sub>H-H</sub> = 4.4 Hz, 2H; β-pyrrole H), 8.25 (d, <sup>3</sup>J<sub>H-H</sub> = 4.7 Hz, 2H; β-pyrrole H), 8.10 (d, <sup>3</sup>J<sub>H-H</sub> = 4.2 Hz, 2H; β-pyrrole H), 6.99 (t, <sup>2</sup>J<sub>H-H</sub> = 7.2 Hz, 3H; *para*-H of PPh<sub>3</sub>), 6.66 (t, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 6H; *meta*-H of PPh<sub>3</sub>), 4.67 (m, 6H; *ortho*-H of PPh<sub>3</sub>); 4.04 (brs, 3H, NH), 3.61 (m, 6H, -CH<sub>2</sub>NH-), 1.79 (m, 6H, alkyl), 1.52 (m, 6H, alkyl), 1.45 (m, 6H, alkyl), 1.38 (m, 12H, alkyl), 0.96 (m, 9H, alkyl). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 470 MHz): -142.23 (dd, *J* = 23.8 Hz, *ortho*-F), -142.59 (dd, *J* = 23.1 Hz, *ortho*-F), -163.10 (m, *meta*-F). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 202 MHz): 27.94. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ in nm (ε in M<sup>-1</sup>cm<sup>-1</sup>): 409 (20500), 551 (3580), 583 (3140); MS: *m/z*: C<sub>76</sub>H<sub>71</sub>CoF<sub>12</sub>N<sub>7</sub>P; [M+H]<sup>+</sup>: 1400.4715; obtained: 1400.4715, [M+H-(PPh<sub>3</sub>)]<sup>+</sup>: 1138.3815; obtained: 1138.3802.

**3** was obtained in 68% yield (29 mg; 18 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ in ppm): 8.59 (d, <sup>3</sup>J<sub>H-H</sub> = 4.7 Hz, 2H; β-pyrrole H), 8.33 (d, <sup>3</sup>J<sub>H-H</sub> = 4.7 Hz, 2H; β-pyrrole H), 8.25 (d, <sup>3</sup>J<sub>H-H</sub> = 4.7 Hz, 2H; β-pyrrole H), 8.12 (d, <sup>3</sup>J<sub>H-H</sub> = 4.7 Hz, 2H; β-pyrrole H), 6.99 (t, <sup>2</sup>J<sub>H-H</sub> = 7.4 Hz, 3H; *para*-H of PPh<sub>3</sub>), 6.67 (t, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 6H; *meta*-H of PPh<sub>3</sub>), 4.69 (m, 6H; *ortho*-H of PPh<sub>3</sub>); 4.06 (brs, 3H, NH), 3.62 (m, 6H, -CH<sub>2</sub>NH-), 1.79 (m, 6H, alkyl), 1.52 (m, 8H, alkyl), 1.44 (m, 6H, alkyl), 1.32 (40H, alkyl), 0.91 (m, 9H, alkyl). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 470 MHz): -140.29 (dd, *J* = 23.3 Hz, *ortho*-F), -140.65 (dd, *J* = 23.3 Hz, *ortho*-F), -141.46 (dd, *J* = 23.3 Hz, *ortho*-F), -141.95 (dd, *J* = 23.3 Hz, *ortho*-F), -160.64 (m, *meta*-F); -160.20 (m, *meta*-F). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 202 MHz): 29.91. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ in nm (ε in M<sup>-1</sup>cm<sup>-1</sup>): 409 (84300), 551 (14700), 584 (12800); MS: *m/z*: C<sub>91</sub>H<sub>101</sub>CoF<sub>12</sub>N<sub>7</sub>P; [M+H-(PPh<sub>3</sub>)]<sup>+</sup>: 1348.6163; obtained: 1348.6143.

### Preparation of electrode - Coating of the ink on the carbon paper:

Coating of the 1 mM ink on 1 cm<sup>2</sup> of carbon paper was done with an automatic pipettor, followed by air drying for 30 m. All studies used 100 μL of ink, with the exception of ICP studies, which used 400 μL. Coating of the 3 mM ink on the carbon paper was done with a Master Performance G233 Pro airbrush. The airbrush was loaded with 1 mL of the ink and a 0.3 mm needle was used to spray-coat 4 x 1 cm<sup>2</sup> of carbon paper simultaneously, before air drying for 30 m. The “as prepared electrode”, wherever mentioned, means that catalytic LSVs were performed until a constant current-voltage profile was obtained (three to ten scans).

## Conversion of Hg/HgO potential to RHE

A Hg/HgO electrode has been used as the reference electrode for alkaline water splitting reactions. The internal solution within Hg/HgO is 1 M KOH. All the potential values obtained with respect to Hg/HgO have been converted to RHE (reversible hydrogen electrode), using the Nernst Equation as described below.<sup>4</sup>

$$E_{RHE} = E_{Hg/HgO} + \left(2.303 + \frac{RT}{F}\right) \times pH + E_{Hg/HgO}^0$$

Where  $E_{Hg/HgO}$  is the potential measured with Hg/HgO as the reference electrode,  $R$  is the ideal gas constant ( $8.31432 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ),  $T$  is temperature (298.15 K),  $F$  is Faraday's constant ( $96485 \text{ C}\cdot\text{mol}^{-1}$ ),  $E_{Hg/HgO}^0$  is the half-cell standard reduction potential of the Hg/HgO electrode [0.0983 V vs SHE (standard hydrogen electrode) at 25°C].<sup>5</sup> For a 1 M KOH solution, pH is 14. Thus, the equation reduces to

$$E_{RHE} = E_{Hg/HgO} + 0.9271$$

## Preparation of ICP-OES samples

A 1 cm<sup>2</sup> area of carbon paper was coated with 400 μL of 1 mM ink solution using an automatic pipettor and allowed to air dry for 20 mins. For each set of catalysts, data was collected for three conditions: (1) after obtaining LSVs; (2) after chronoamperometry conditions at -10 mA and -50 mA for the HER; (3) after 10 mA and 50 mA for the OER. The electrode (carbon paper coated with ink) was first heated in concentrated HNO<sub>3</sub> for 20 m. The pale pink acid solution was then transferred into a measuring cylinder and the volume made up with deionized water to 10 mL and filtered with 25 mm syringe filter, 0.45 μm PTFE.

## Calculation of TOF

The turnover frequency TOF, was calculated as per the following equation:

$$TOF = \frac{I}{n \times F \times m}$$

Where  $I$  is the current,  $F$  is Faraday's constant,  $m$  is the moles of the catalyst (as calculated from ICP data), and  $n$  is number of electrons transferred to generate one molecule of the product. Thus,  $n = 2$  for HER and 4 for OER.<sup>6</sup>



**Table S1:** Calculation of TOF for **1, 2 and 3** with the values obtained from ICP-OES measurements for as prepared electrodes for HER and OER.

Catalyst	Ink conc	$\eta$ (V)	$I$ (mA)	$n$	$F$	$m$	TOF (s <sup>-1</sup> )
1: HER	1 mM	1.08	0.03	2	96485	$3.76 \times 10^{-7}$	0.413
2: HER	1 mM	1.08	0.06	2	96485	$3.11 \times 10^{-7}$	1.02
3: HER	1 mM	1.08	0.085	2	96485	$1.48 \times 10^{-7}$	2.98
1: OER	1 mM	0.59	0.025	4	96485	$3.83 \times 10^{-7}$	0.169
2: OER	1 mM	0.59	0.04	4	96485	$3.44 \times 10^{-7}$	0.301
3: OER	1 mM	0.59	0.058	4	96485	$1.35 \times 10^{-7}$	1.11
1: HER	3 mM	1.08	0.067	2	96485	$4.40 \times 10^{-7}$	0.789
2: HER	3 mM	1.08	0.008	2	96485	$7.53 \times 10^{-7}$	0.055
3: HER	3 mM	1.08	0.023	2	96485	$9.58 \times 10^{-7}$	0.124
1: OER	3 mM	0.59	0.037	4	96485	$4.07 \times 10^{-7}$	0.236
2: OER	3 mM	0.59	0.023	4	96485	$6.30 \times 10^{-7}$	0.095
3: OER	3 mM	0.59	0.024	4	96485	$9.54 \times 10^{-7}$	0.065

### Preparation of SEM-EDS samples

A 1 cm<sup>2</sup> area of carbon paper was coated with 100  $\mu$ L of 1 mM ink solution with the help of a autopipetter and allowed to air dry for 20 m. For each set of catalysts, data was collected for three conditions: (1) after obtaining LSVs; (2) after chronoamperometry conditions at  $-10$  mA and  $-50$  mA for the HER; (3) after 10 mA and 50 mA for the OER. The electrode (carbon paper with coated ink) was then sonicated with 15 mL deionized water to remove excess potassium from the surface before imaging.

### Preparation of TEM samples

100  $\mu$ L of 1mM ink solution was coated on 1 cm<sup>2</sup> area of carbon paper with the help of a pipette and allowed to dry for 20 mins. For each set of catalysts, data was collected for three conditions: (1) after obtaining LSVs; (2) after chronoamperometry conditions at  $-10$  mA and  $-50$  mA for the HER; (3) after 10 mA and 50 mA for the OER. The electrode (carbon paper with coated ink) was then sonicated in isopropanol for 10 mins.

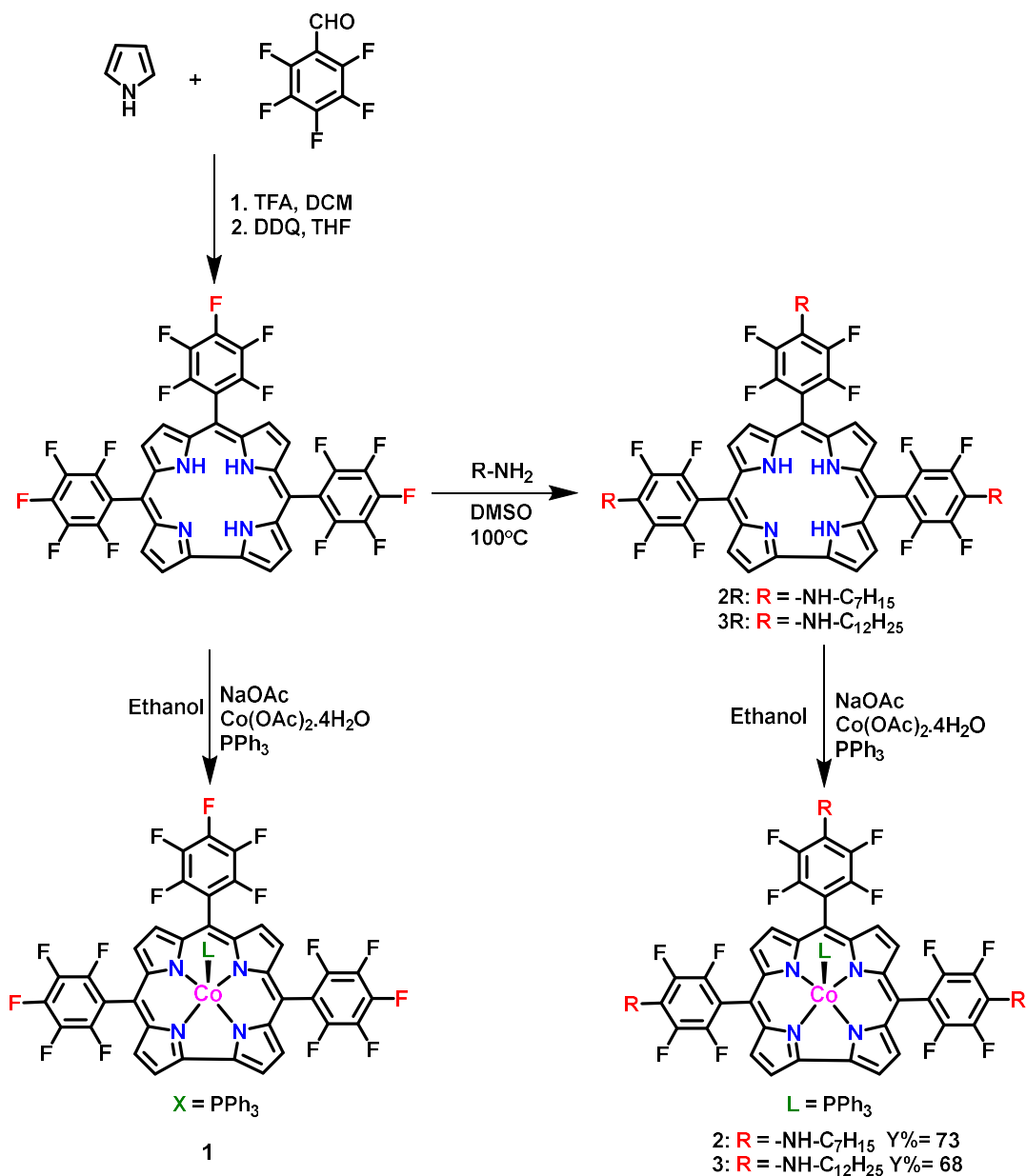
### Tafel Studies

First, LSV scans were obtained until a constant current-voltage response was obtained (2 to 7 scans, on average). The potential at which the catalytic current reaches  $\pm 10$  mA/cm<sup>2</sup> was selected as the initial point for the chronoamperometry studies. Beginning at this potential, chronoamperometry was recorded for 180 s, at which point the observed current had plateaued. Next, the potential was stepped at 20 mV intervals more negative for HER or more positive for OER and the process repeated to obtain 10 total measurements.

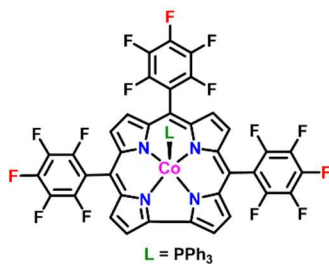
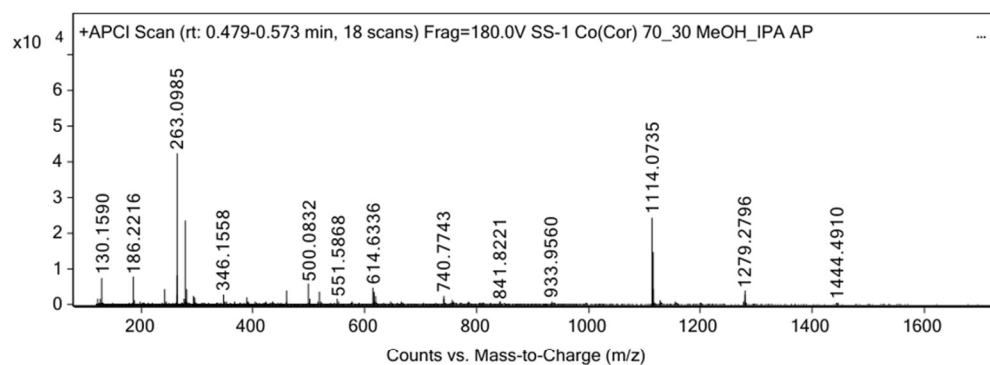
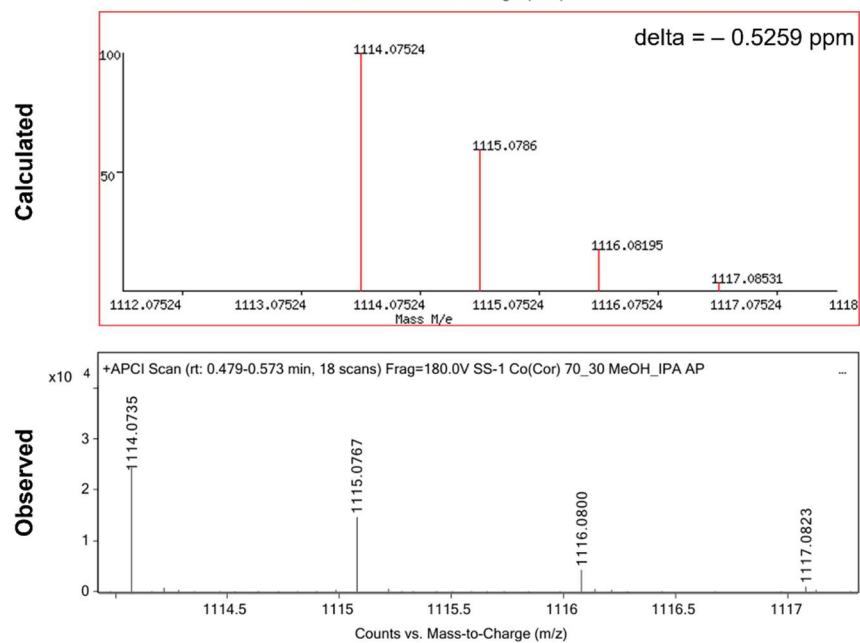
## Water contact angle measurement

A given electrode (carbon paper coated with the catalyst ink), was taped on a platform and a syringe with 0.5 mm diameter was used to deposit a water droplet volume of about 40  $\mu\text{L}$ . Each of the measurements were repeated twice to confirm the reproducibility of the obtained values. Blanks were recorded of carbon paper coated with ink, without catalyst as well as uncoated carbon paper. A Fastec IL5 camera with objective lens with pylon Viewer software was used for recording images and HAYEAR software was used for the angle measurement.

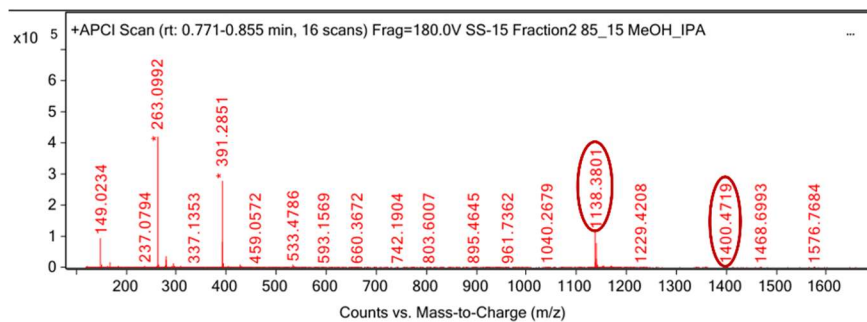
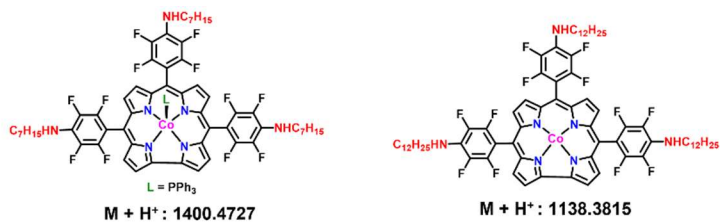
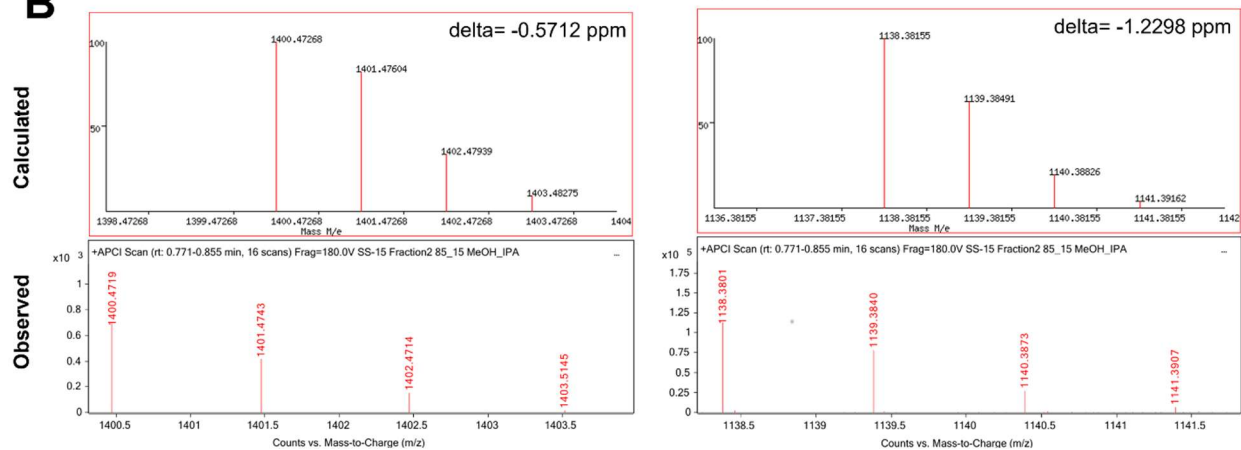
## Synthesis and Characterization



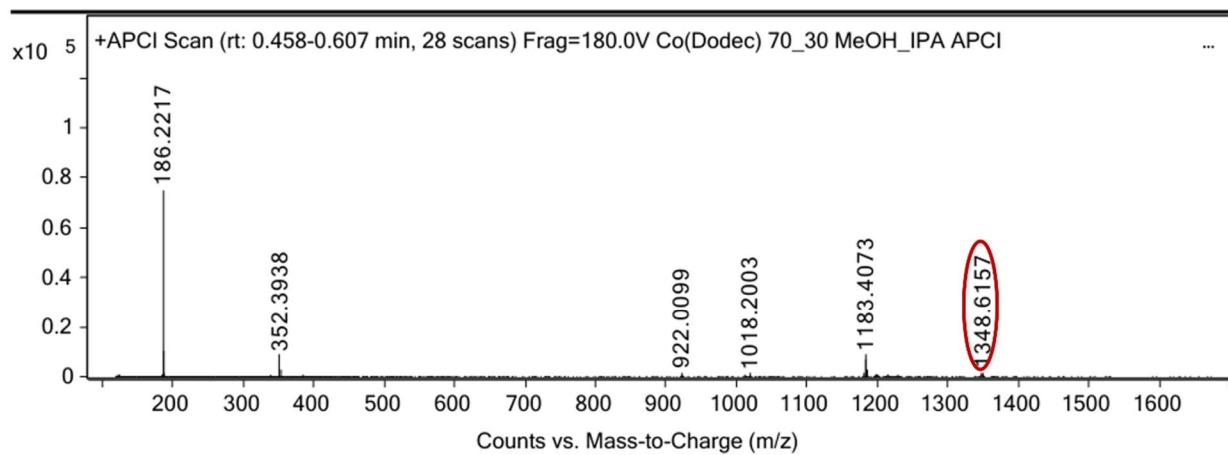
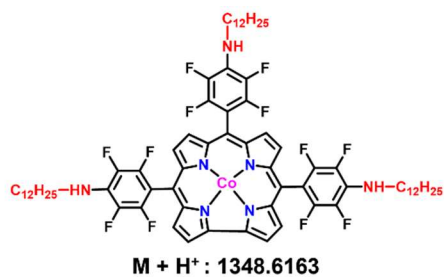
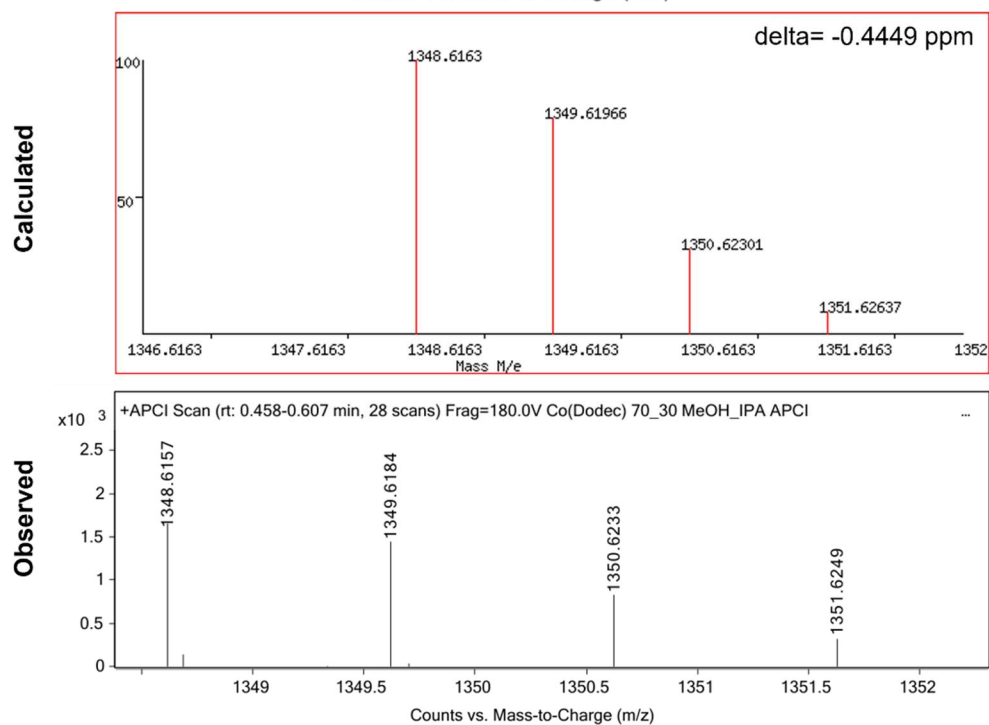
**Scheme 1:** Synthesis of metallocorroles 1-3.

**A****M<sup>+</sup> : 1114.0752****B**

**Figure S1.** HRMS results for **1**; (A) full spectrum; (B) calculated and observed isotopic patterns.

**A****B**

**Figure S2.** HRMS results for **2**; (A) full spectrum; (B) calculated and observed isotopic patterns.

**A****B**

**Figure S3.** HRMS results for **3**; (A) full spectrum; (B) calculated and observed isotopic patterns.

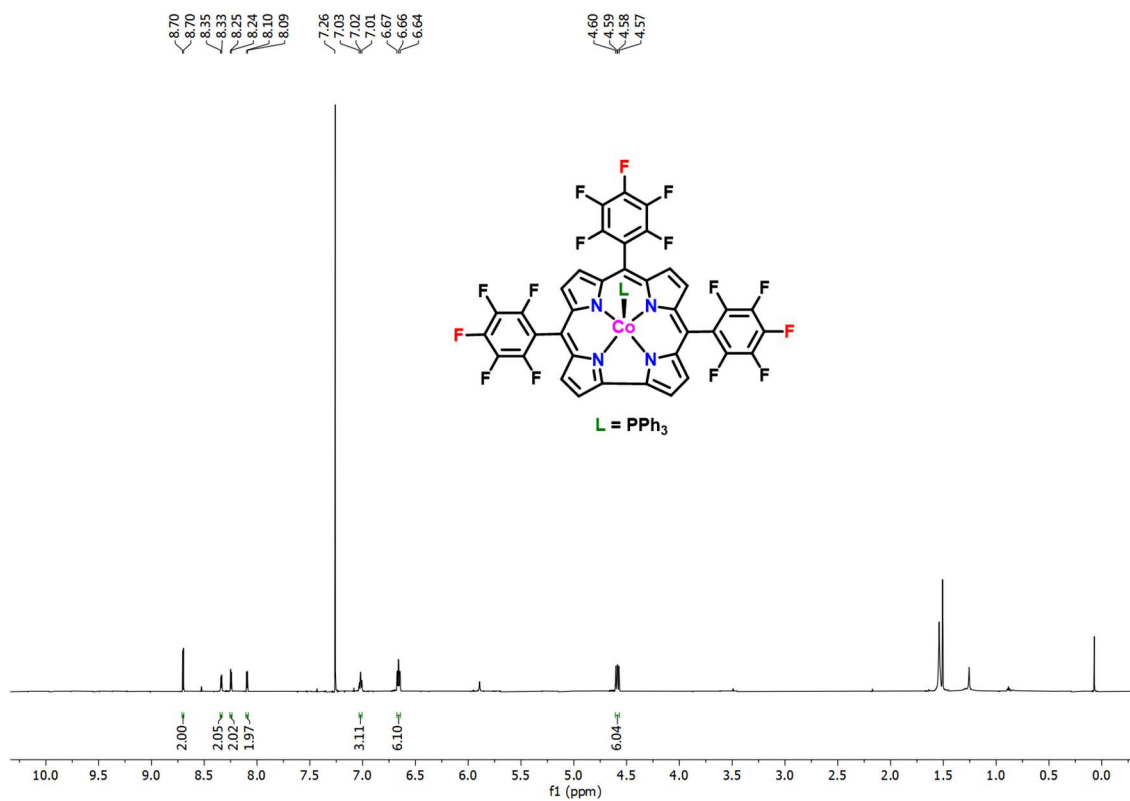


Figure S4.  $^1H$  NMR of **1**, recorded in  $CDCl_3$ , 500 MHz.

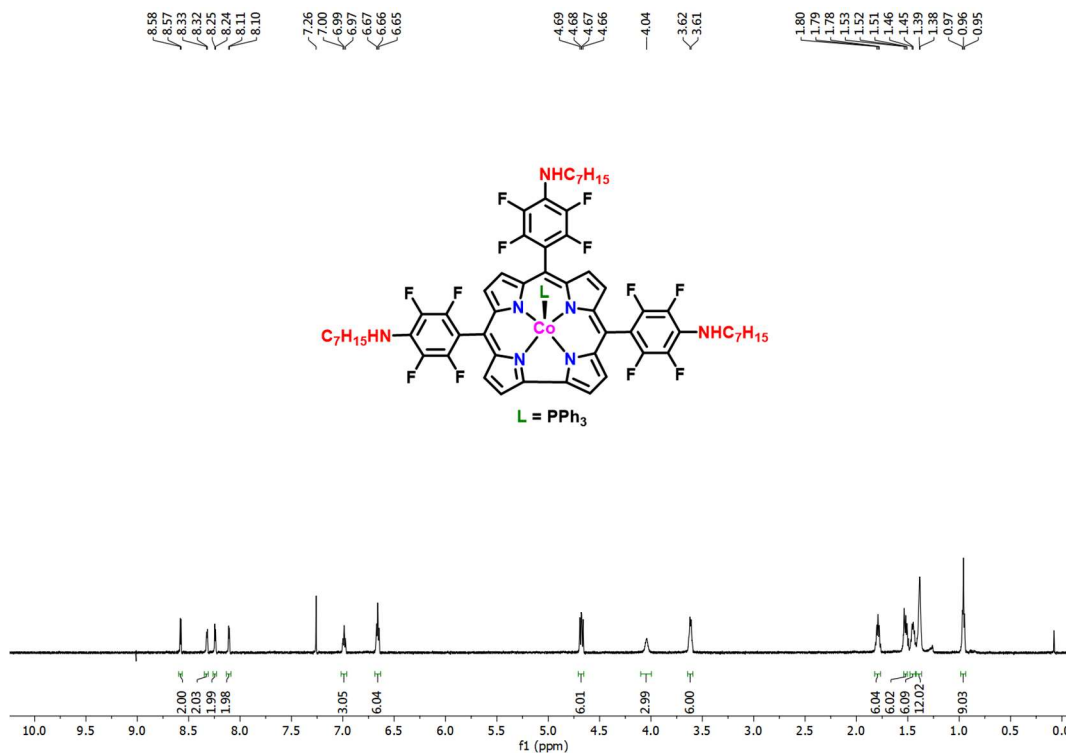
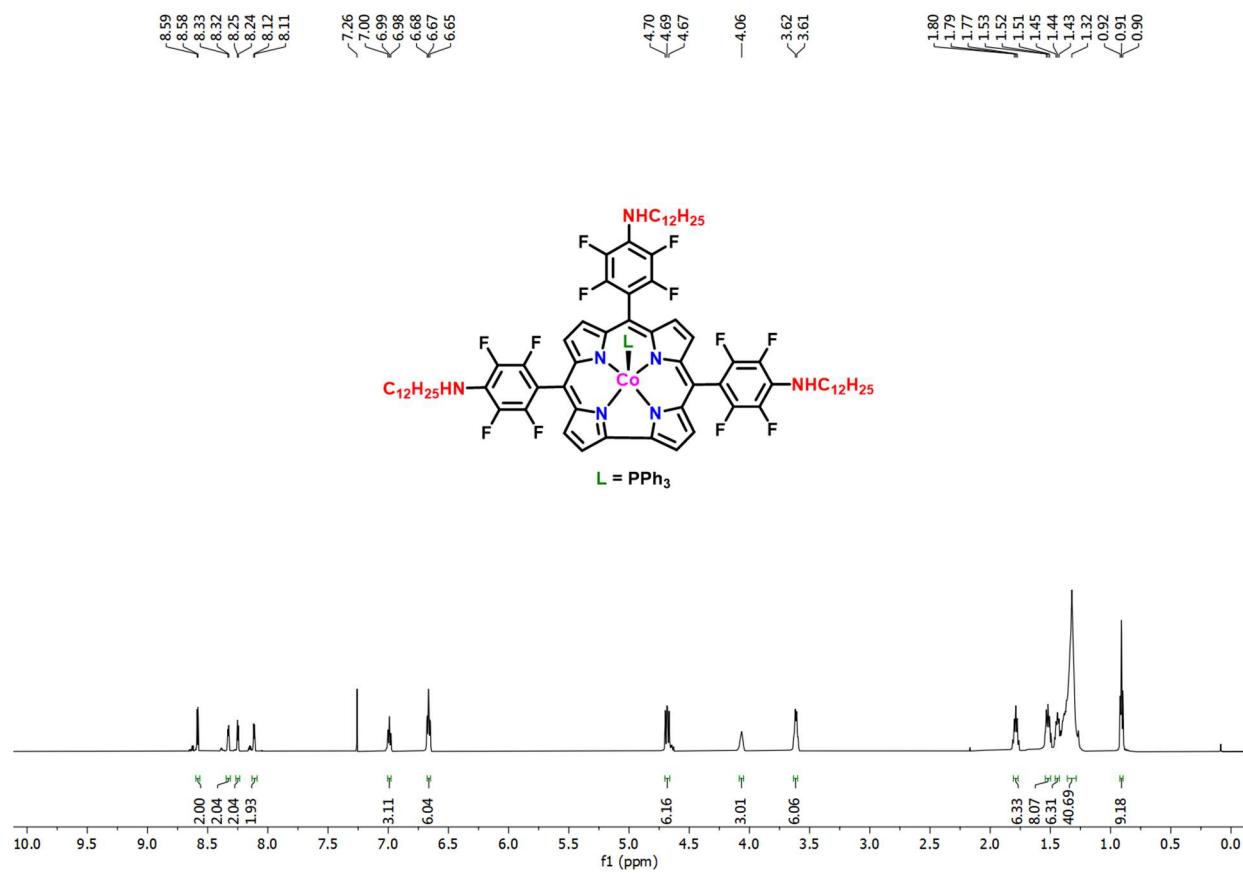
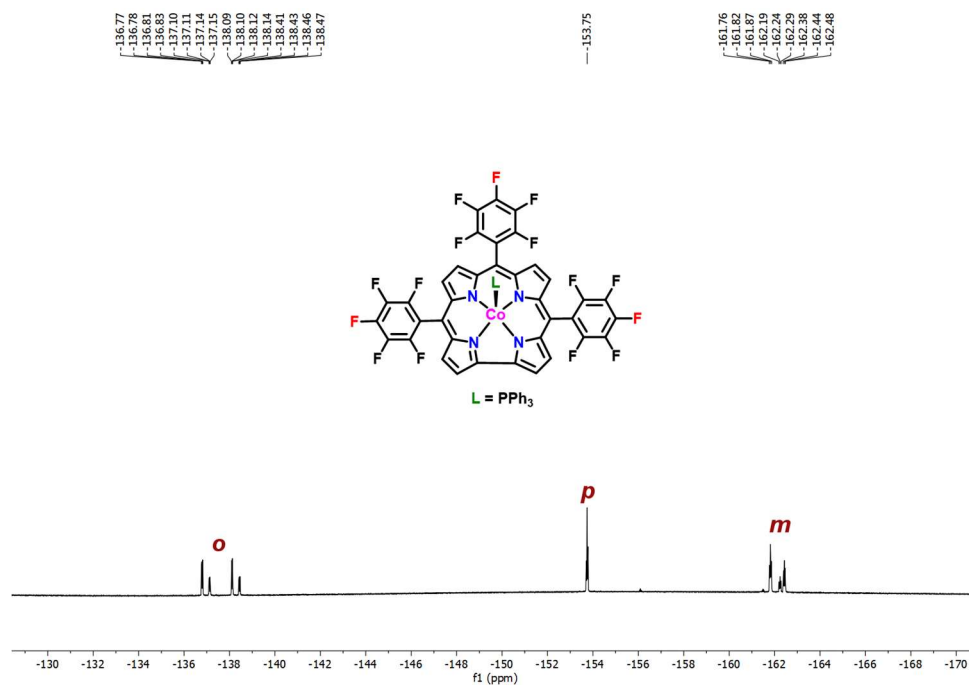


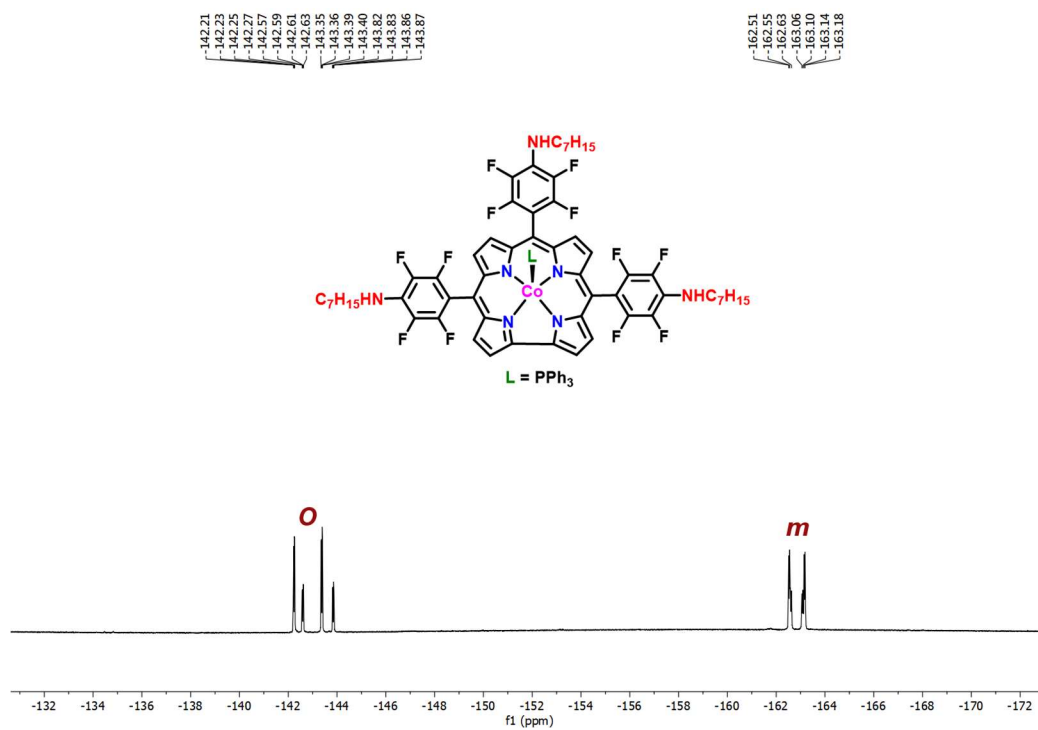
Figure S5.  $^1H$  NMR of **2**, recorded in  $CDCl_3$ , 500 MHz.



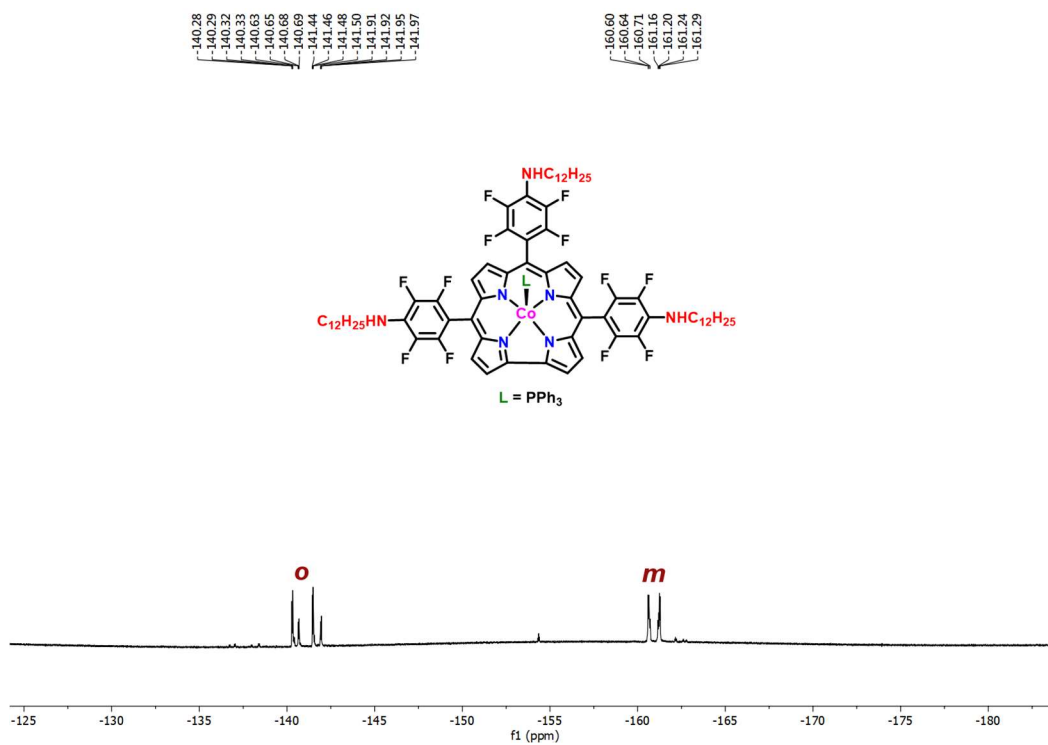
**Figure S6.**  $^1\text{H}$  NMR of **3**, recorded in  $\text{CDCl}_3$ , 500 MHz.



**Figure S7.**  $^{19}\text{F}$  NMR of **1**, recorded in  $\text{CDCl}_3$ , 470 MHz

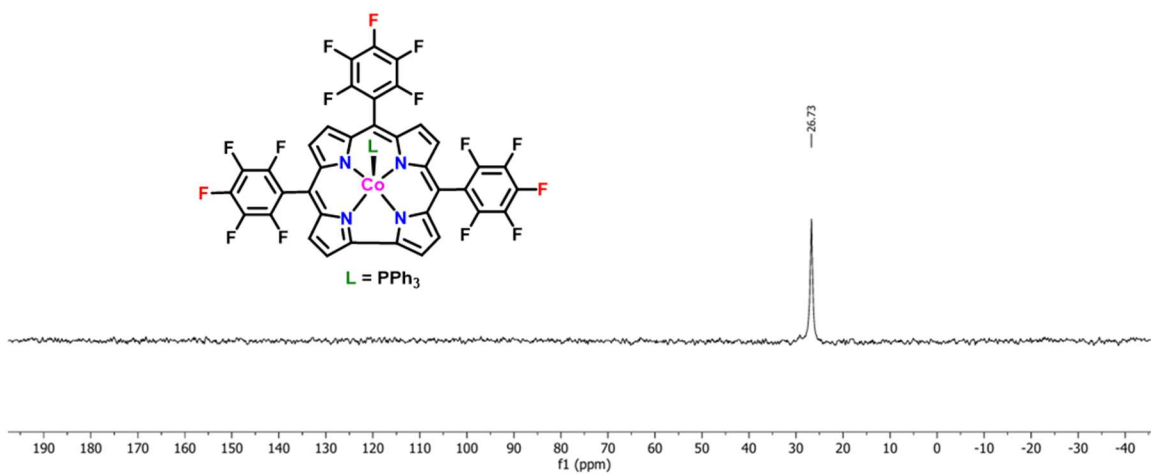


**Figure S8.**  $^{19}F$  NMR of **2**, recorded in  $CDCl_3$ , 470 MHz

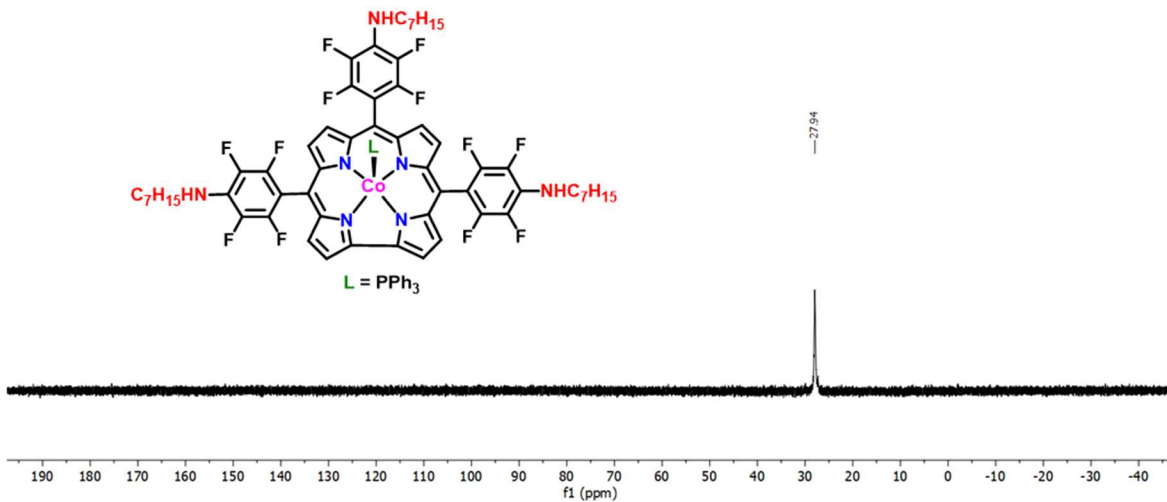


**Figure S9.**  $^{19}F$  NMR of **3**, recorded in  $CDCl_3$ , 470 MHz.

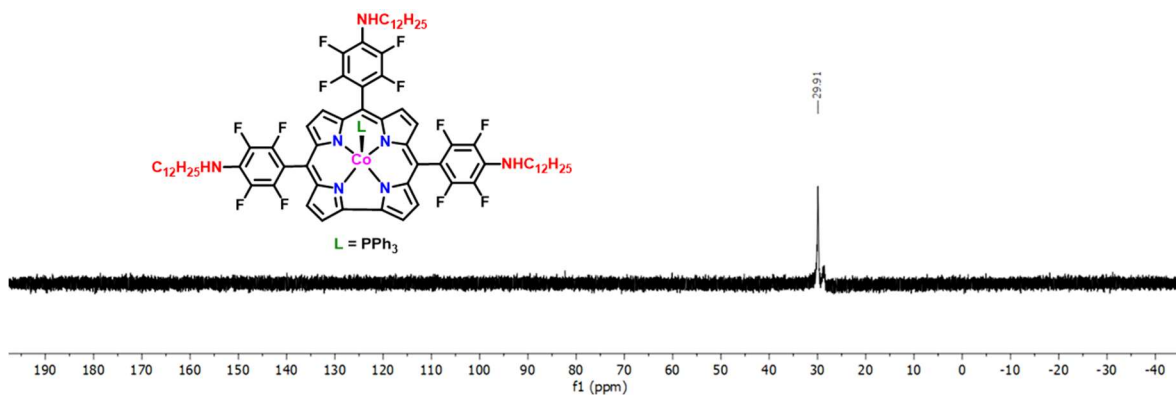




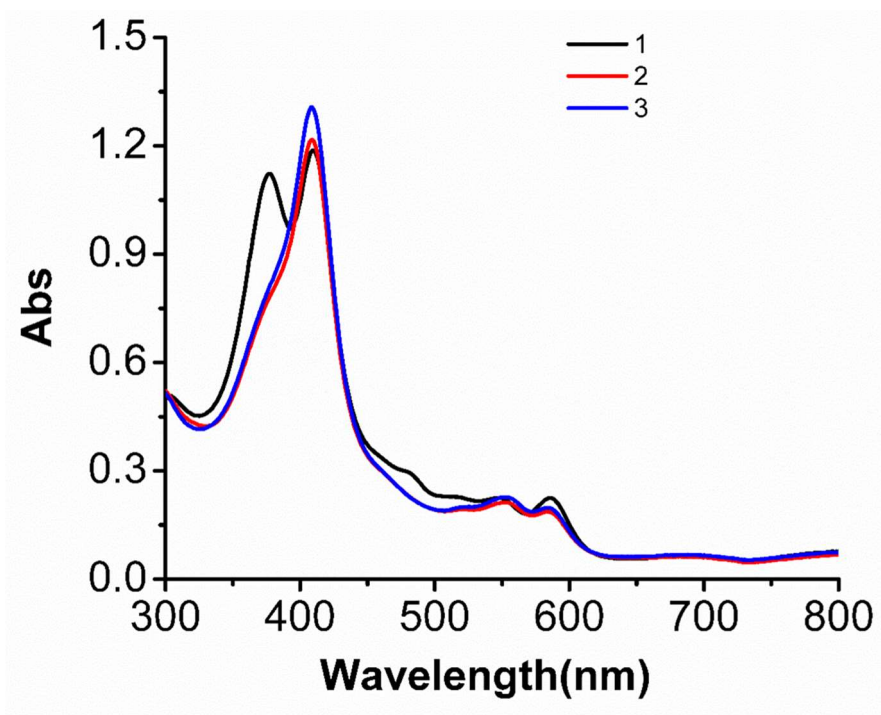
**Figure S10.**  $^{31}\text{P}$  NMR of **1**, recorded in  $\text{CDCl}_3$ , 202 MHz.



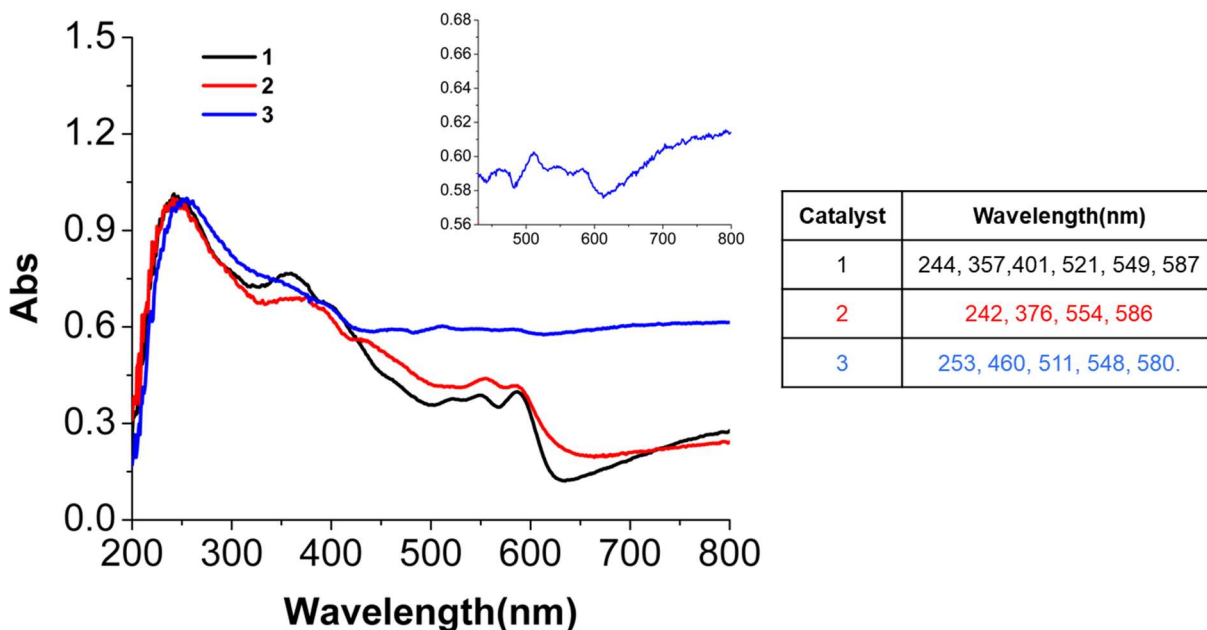
**Figure S11.**  $^{31}\text{P}$  NMR of **2**, recorded in  $\text{CDCl}_3$ , 202 MHz.



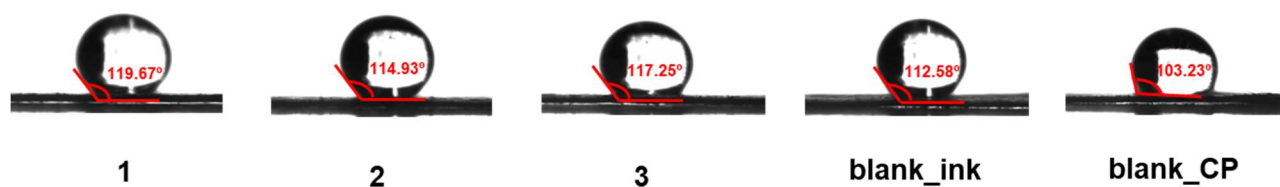
**Figure S12.**  $^{31}\text{P}$  NMR of **3**, recorded in  $\text{CDCl}_3$ , 202 MHz.



**Figure S13.** UV-vis data of **1-3**, recorded in CH<sub>2</sub>Cl<sub>2</sub>. Conditions: concentrations  $1.97 \times 10^{-5}$  M for **1**,  $5.95 \times 10^{-5}$  M for **2**,  $1.55 \times 10^{-5}$  M for **3**; quartz cell with 1 cm pathlength.

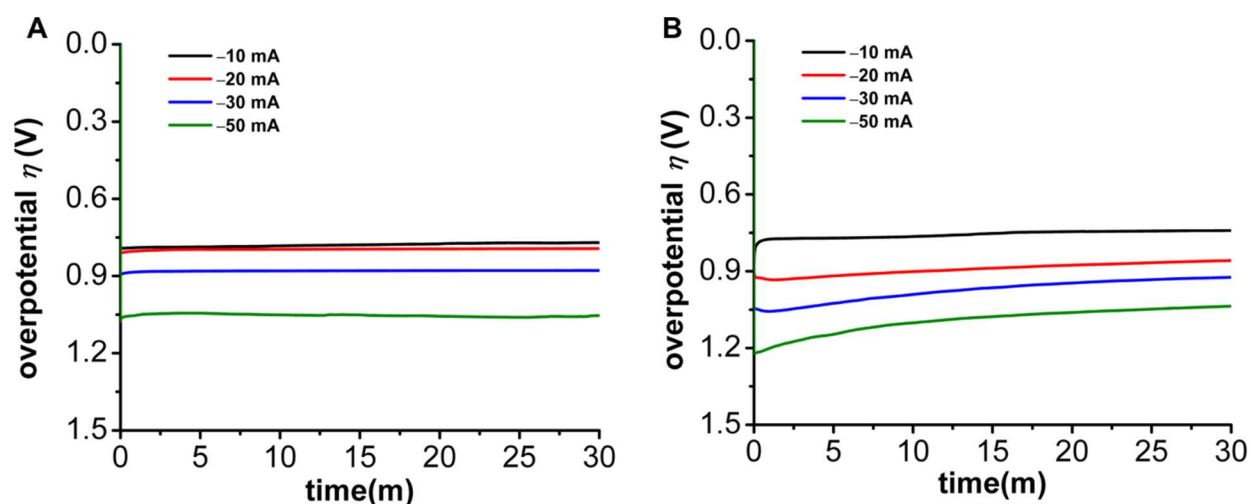


**Figure S14.** Solid-state UV-vis data of **1-3**, ink coated on carbon paper. Ink made with 0.1 mM of catalyst, 0.5 mL of Nafion, 1 mL of ethanol and 3.5 mL of CH<sub>2</sub>Cl<sub>2</sub>. Inset: Expanded view of selected region for **3**.

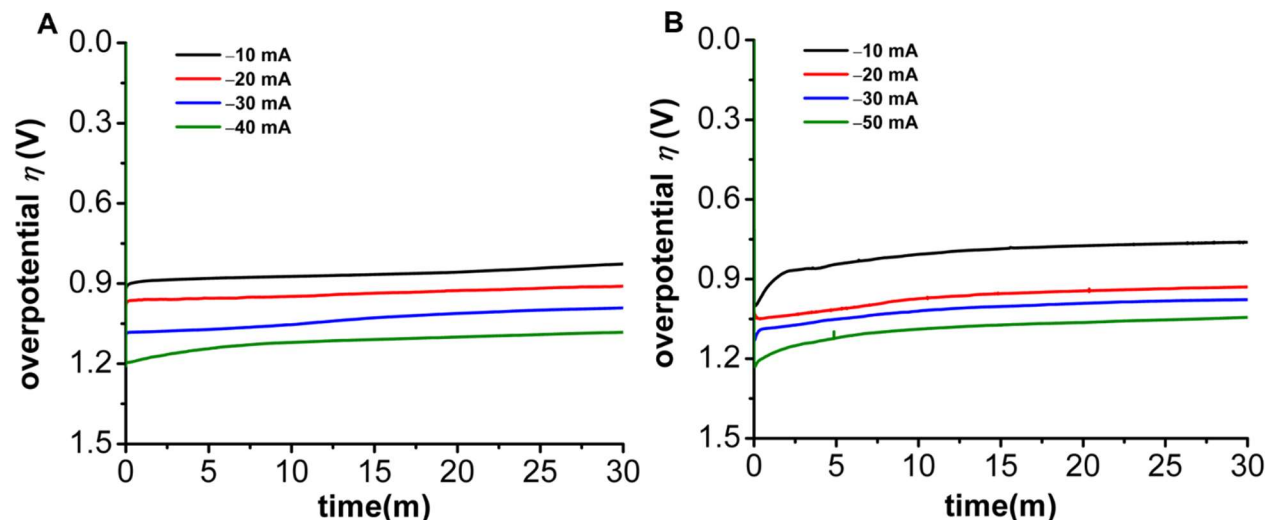


**Figure S15.** Water contact angle measurement for 1, 2, 3, blank\_ink (carbon paper coated with ink without the catalyst) and blank\_CP (carbon paper not coated with ink).

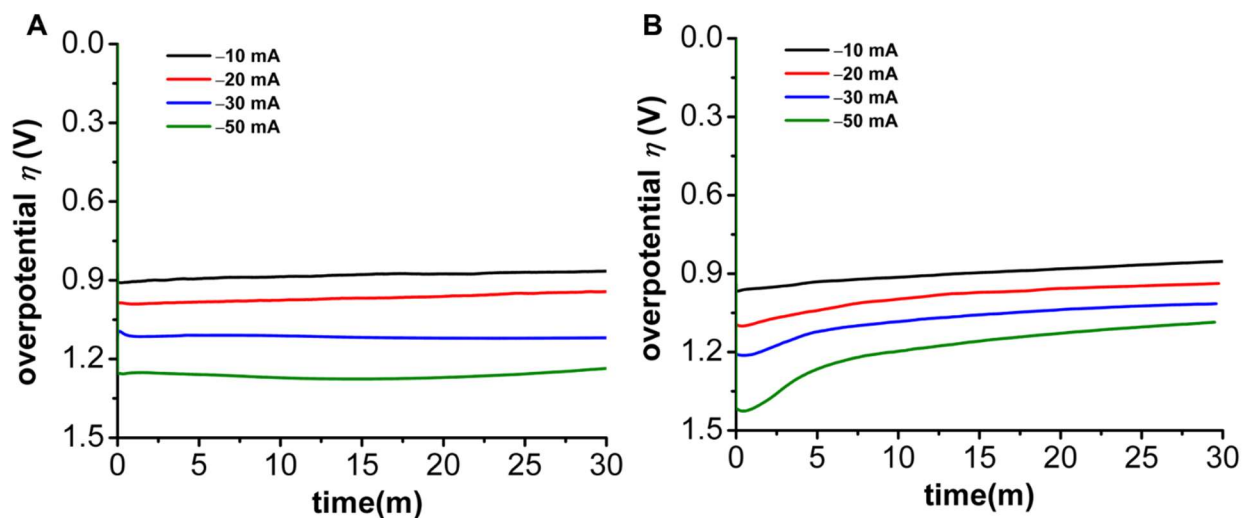
## Electrochemistry



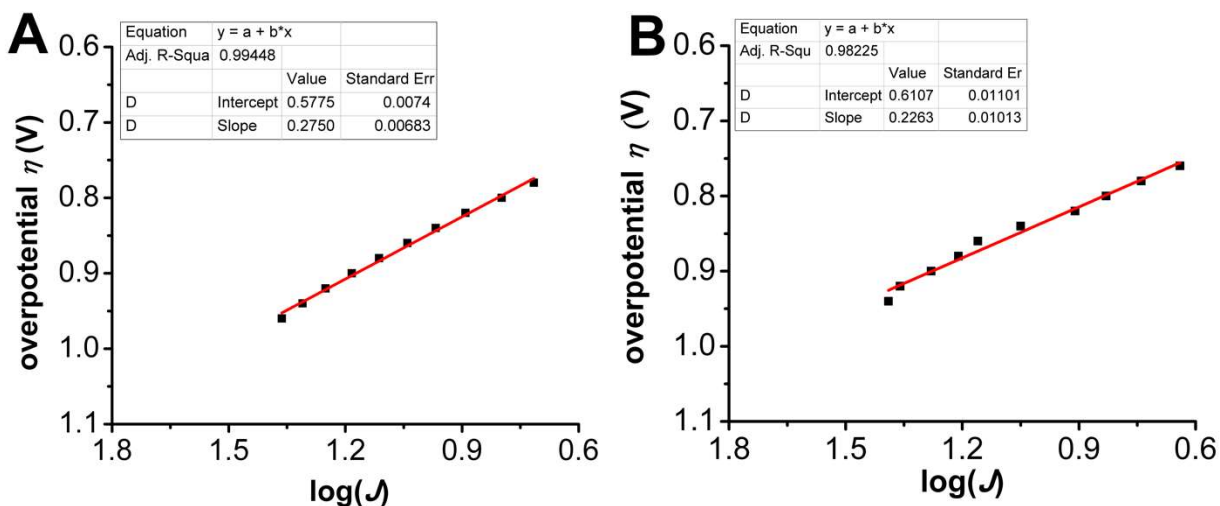
**Figure S16.** Stability tests for HER under chronopotentiometry conditions for **1**, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.



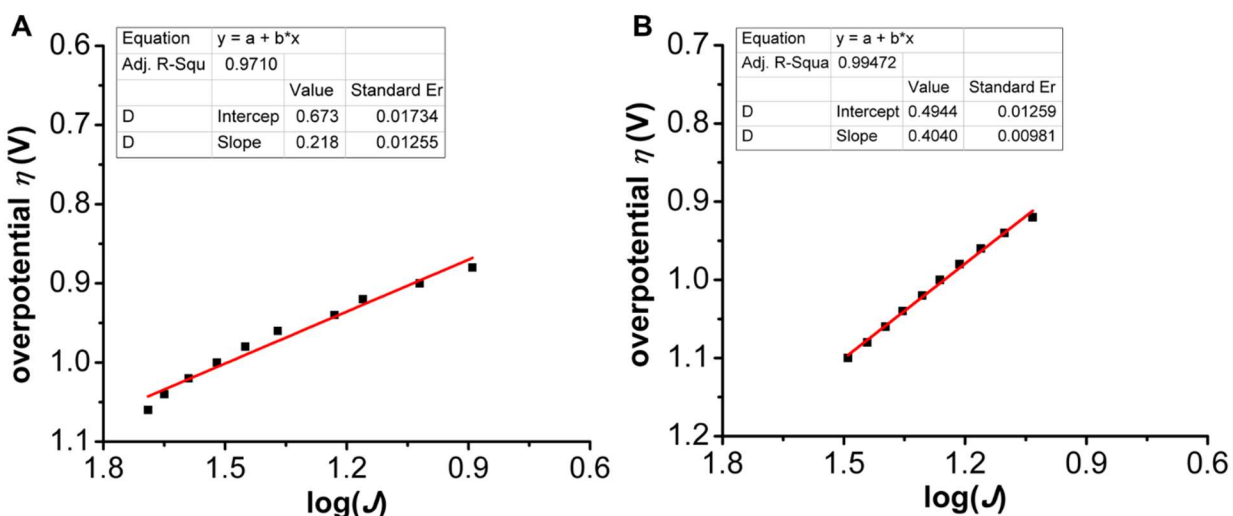
**Figure S17.** Stability tests for HER under chronopotentiometry conditions for **2**, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.



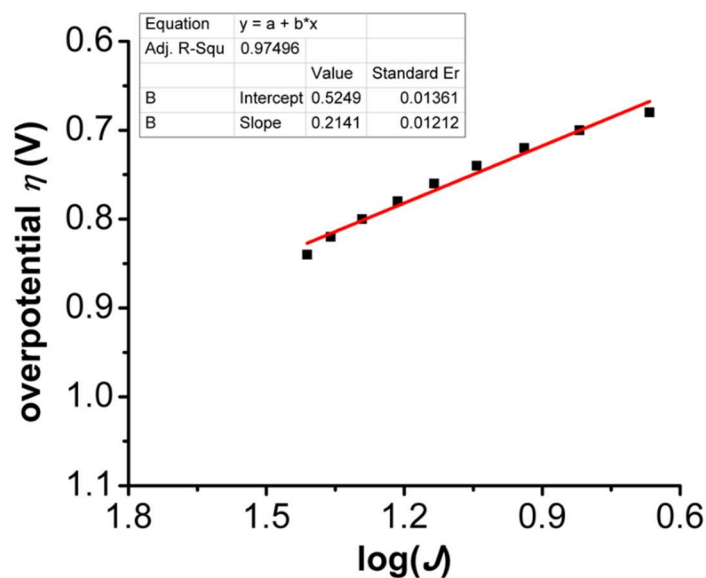
**Figure S18.** Stability tests for HER under chronopotentiometry conditions for **3**, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.



**Figure S19.** Tafel studies of **1** for HER, obtained with 1 cm<sup>2</sup> of carbon paper coated with Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.



**Figure S20.** Tafel studies of **2** for HER, obtained with 1 cm<sup>2</sup> of carbon paper coated with Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.

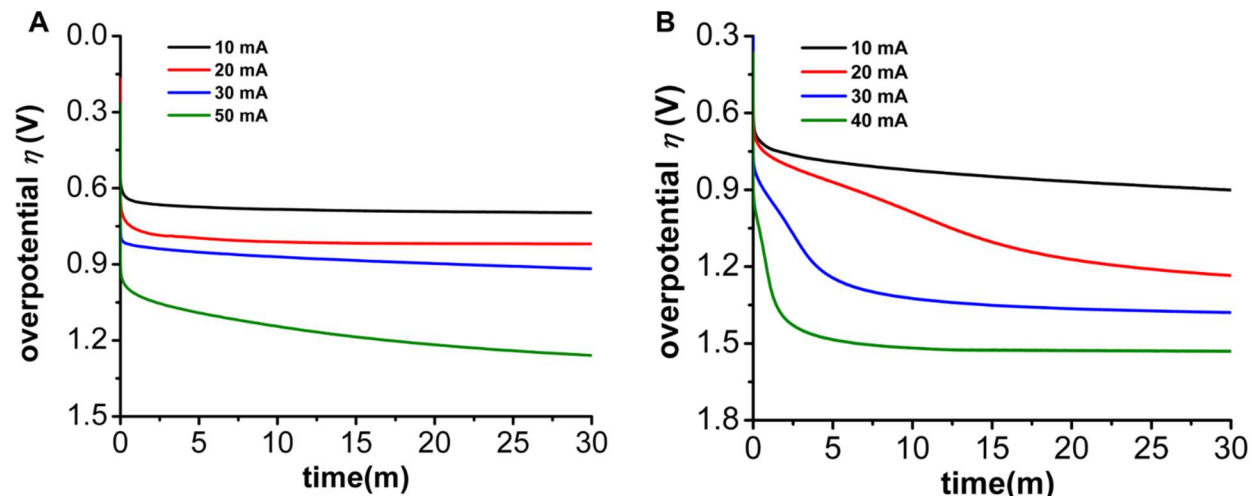


**Figure S21.** Tafel studies of **3** for HER, obtained with 1 cm<sup>2</sup> of carbon paper coated with Vulcan Carbon, Nafion and 1 mM of catalyst, coated by pipette, as working electrode. The experiment was performed under N<sub>2</sub>, in 1.0 M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.

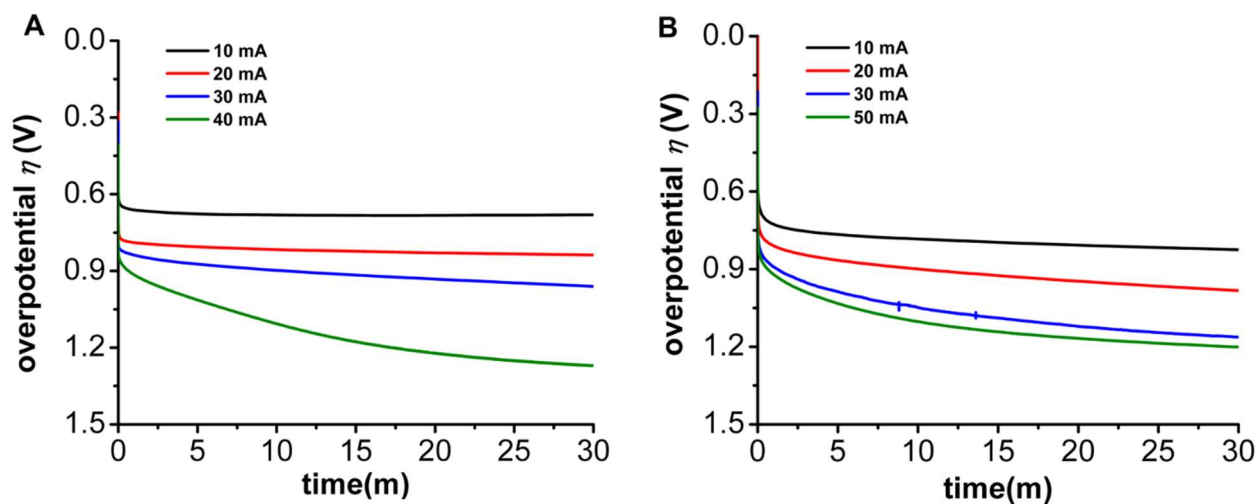
**Table S2.** Comparative summary of HER studies for **1**, **2** and **3** for 1 mM and 3 mM concentration inks.

Compound	Onset Potentials for 1 mM solution vs RHE (V)	Overpotential at 10 mA/cm <sup>2</sup> (V)	Tafel Slopes for 1 mM solution (mV/dec <sup>-1</sup> )	Onset Potentials for 3 mM solution vs RHE (V)	Overpotential at 10 mA/cm <sup>2</sup> (V)	Tafel Slopes for 3 mM solution (mV/dec <sup>-1</sup> )
1	-0.75	0.96	275	-0.67	0.79	226
2	-0.68	0.90	218	-0.78	-	404
3	-0.63	0.86	214	-0.81	0.86	NS

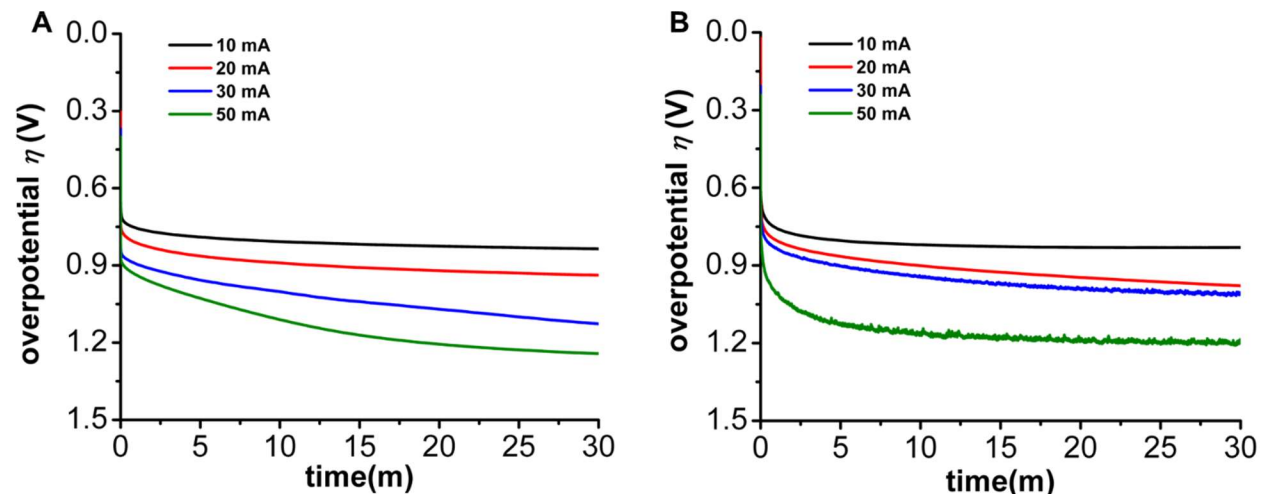
NS: Not stable to be studied under chronoamperometry conditions.



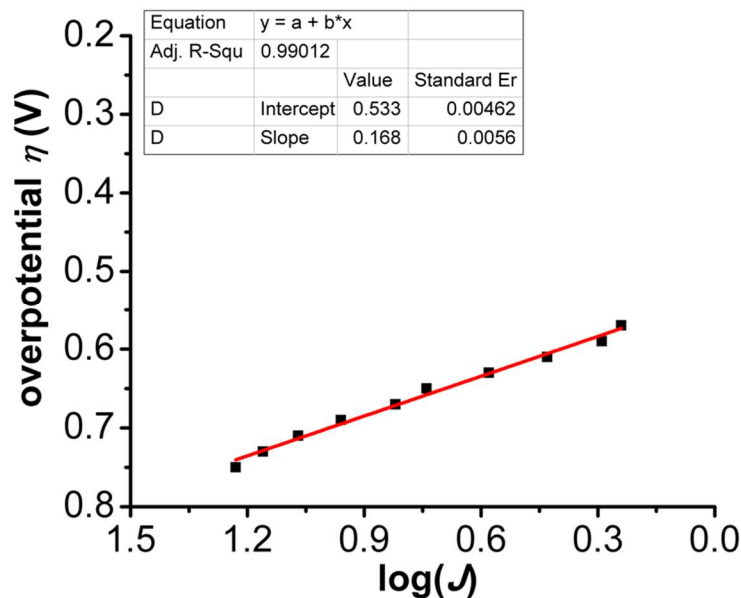
**Figure S22.** Stability tests for OER under chronopotentiometry conditions for **1**, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.



**Figure S23.** Stability tests for OER under chronopotentiometry conditions for **2**, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.

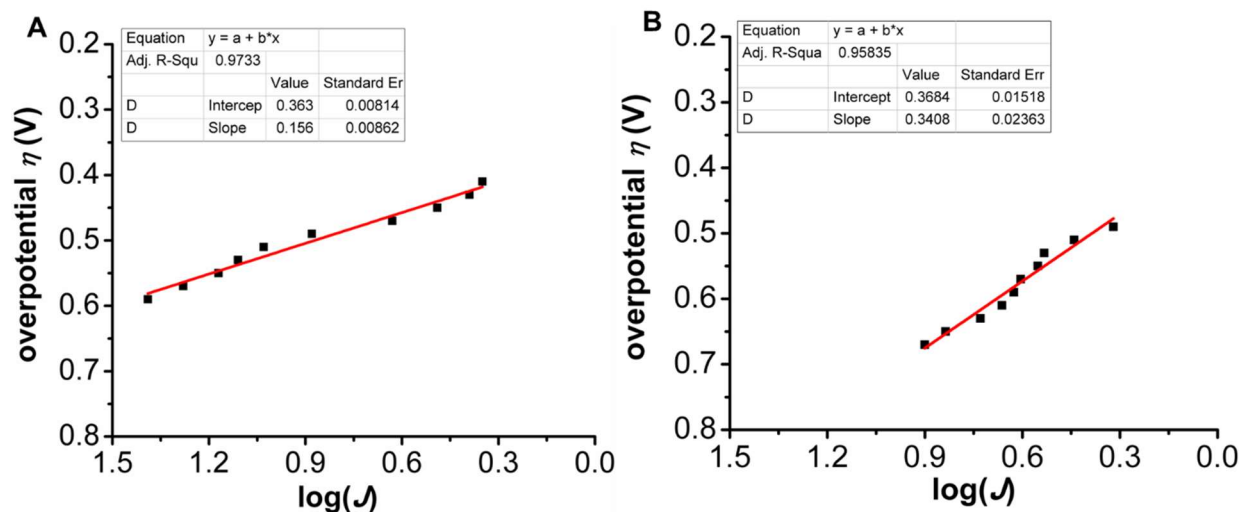


**Figure S24.** Stability tests for OER under chronopotentiometry conditions for **3**, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.

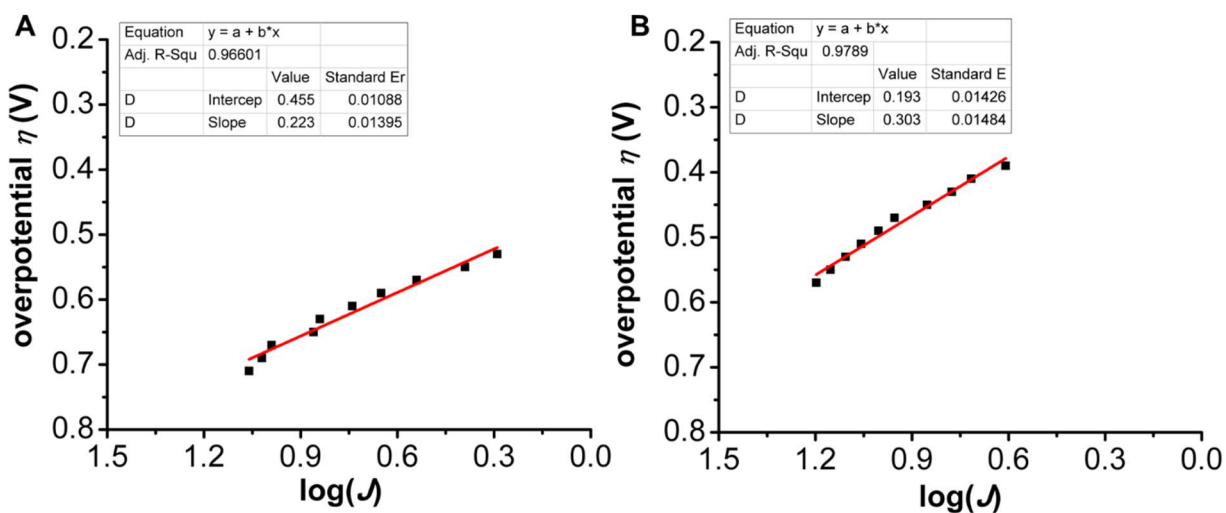


**Figure S25.** Tafel studies of **1** for OER, obtained with 1 cm<sup>2</sup> of carbon paper coated with Vulcan Carbon, Nafion and 1 mM of catalyst, coated by pipette, as working electrode. The experiment was performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.





**Figure S26.** Tafel studies of **2** for OER, obtained with 1 cm<sup>2</sup> of carbon paper coated with Vulcan Carbon, Nafion and catalyst. (A) 1 mM (coated by pipette) and (B) 3 mM (coated by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.

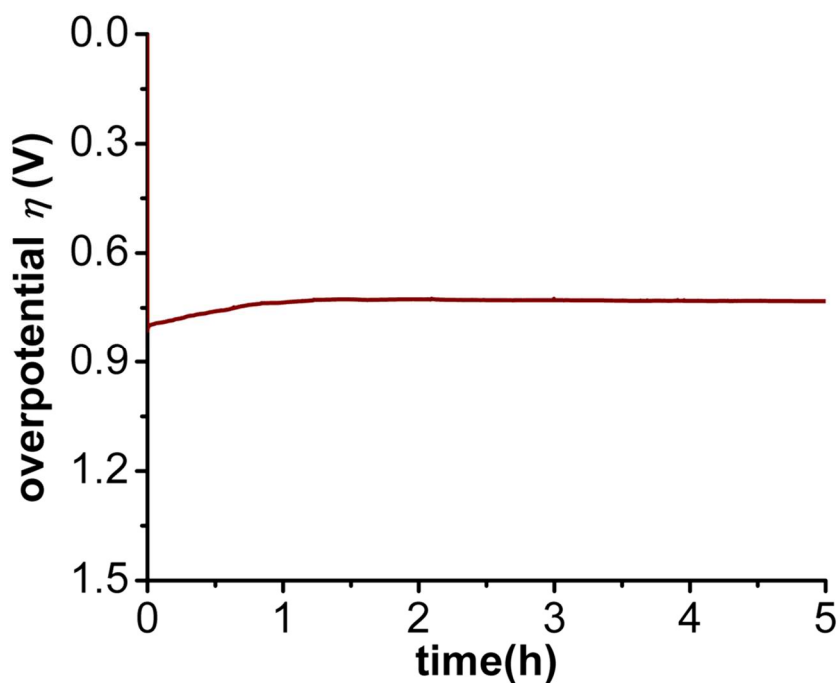


**Figure S27.** Tafel studies of **3** for OER, obtained with 1 cm<sup>2</sup> of carbon paper coated with Vulcan Carbon, Nafion and catalyst (A) 1 mM (coating by pipette) and (B) 3 mM (coating by airbrush) as working electrode. All experiments were performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.

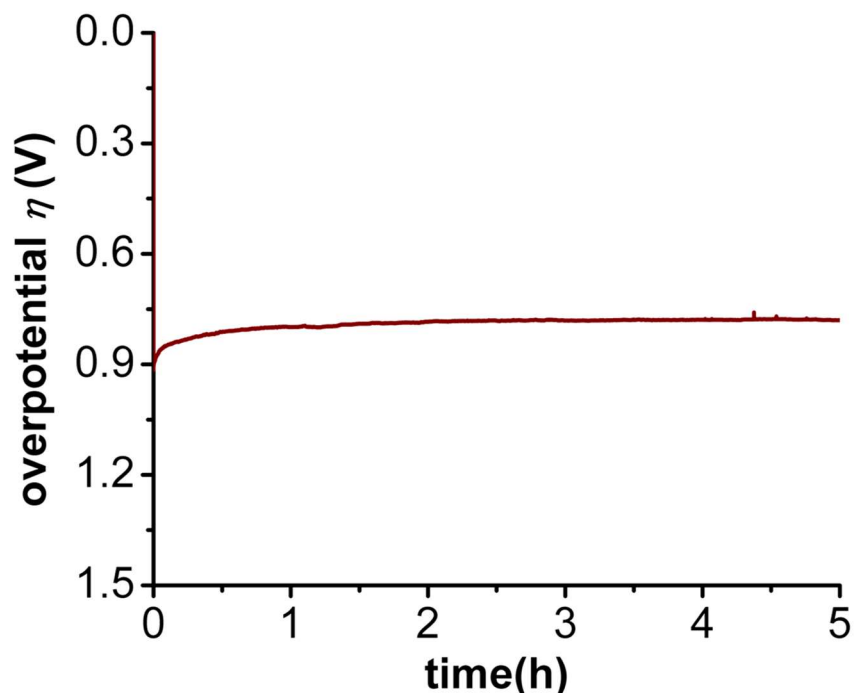
**Table S3.** Comparative summary of OER studies for **1**, **2** and **3** for 1 mM and 3 mM loading inks.

Compound	Onset Potentials for 1 mM solution vs RHE (V)	Overpotential at 10 mA/cm <sup>2</sup> (V)	Tafel Slopes for 1 mM solution (mV/dec <sup>-1</sup> )	Onset Potentials for 3 mM solution vs RHE (V)	Overpotential at 10 mA/cm <sup>2</sup> (V)	Tafel Slopes for 3 mM solution (mV/dec <sup>-1</sup> )
1	1.68	0.56	168	1.54	0.42	NS
2	1.56	0.51	156	1.51	0.52	340
3	1.51	0.46	223	1.63	0.54	303

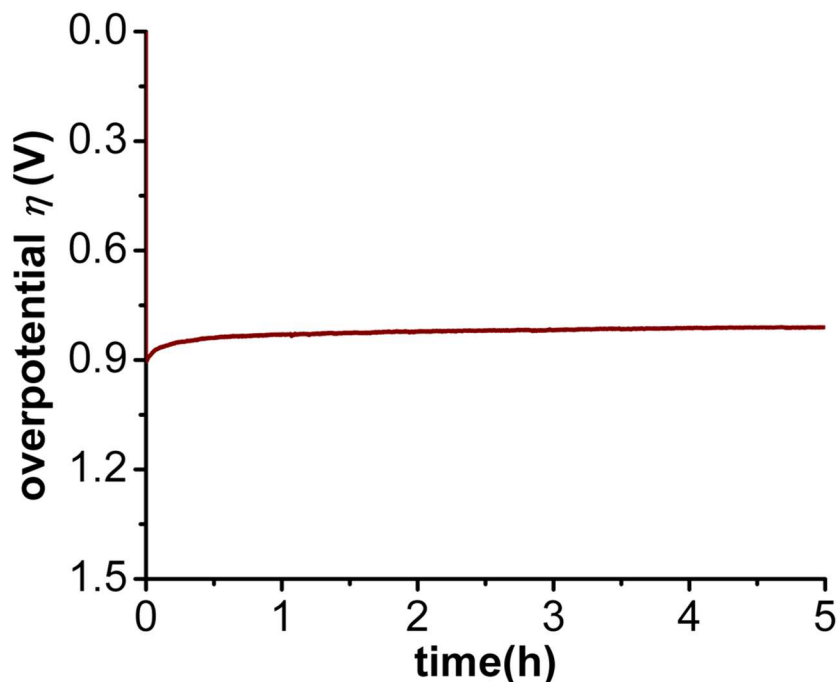
NS: Not stable to be studied under chronoamperometry conditions.



**Figure S28.** Stability tests of **1** for HER, under chronopotentiometry conditions at  $-10$  mA for 5 h, obtained with  $1$  cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and 1.0 mM of catalyst as the working electrode. The experiment was performed under N<sub>2</sub>, in 1.0 M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.



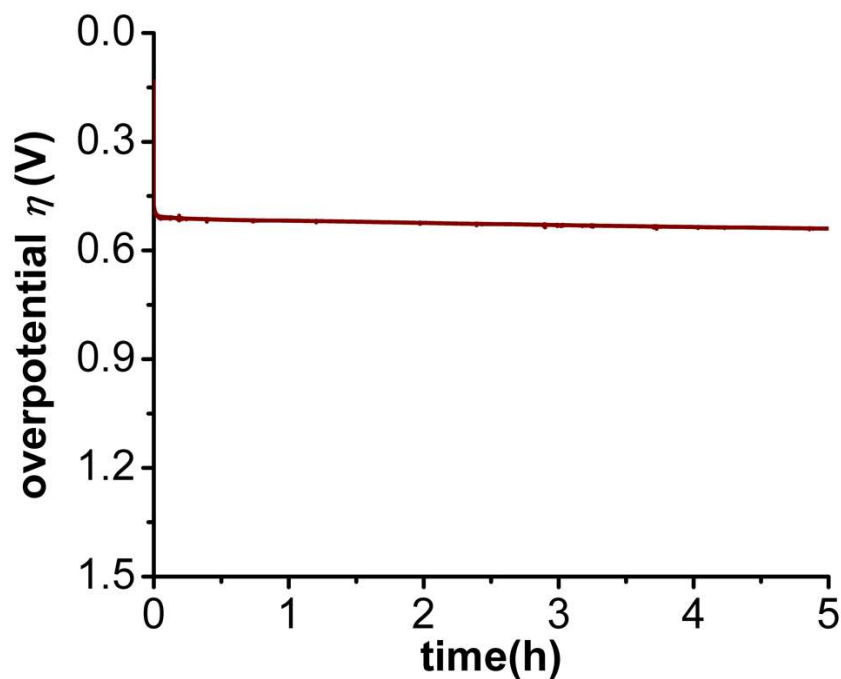
**Figure S29.** Stability tests of **2** for HER, under chronopotentiometry conditions at  $-10$  mA for 5 h, obtained with  $1$  cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and  $1.0$  mM of catalyst as the working electrode. The experiment was performed under N<sub>2</sub>, in  $1.0$  M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode;  $100$  mV/s scan rate.



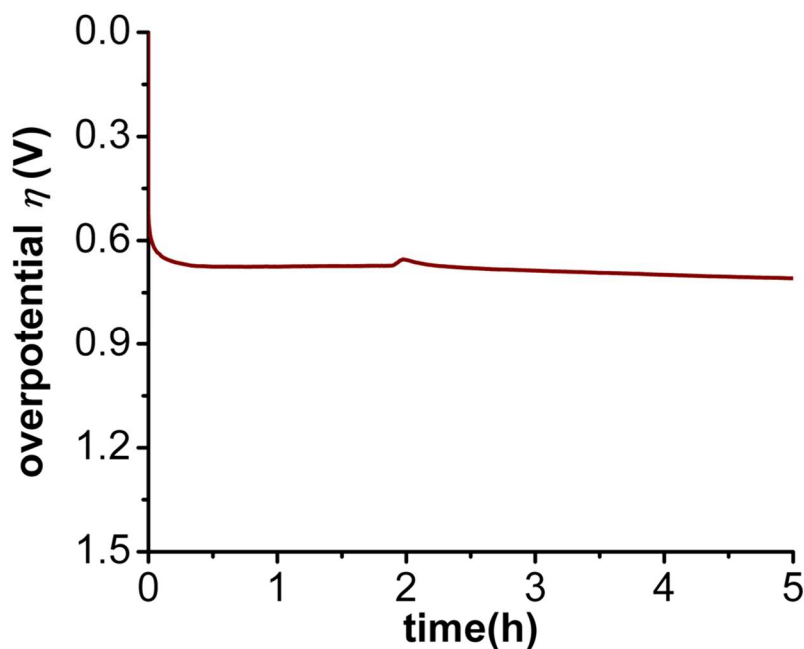
**Figure S30.** Stability tests of **3** for HER, under chronopotentiometry conditions at  $-10$  mA for 5 h, obtained with  $1$  cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and  $1.0$  mM of catalyst as the working electrode. The experiment was performed under N<sub>2</sub>, in  $1.0$  M KOH; Glassy carbon counter electrode, Hg/HgO reference electrode;  $100$  mV/s scan rate.

**Table S4.** Calculations for change of overpotential over time for stability tests for HER of catalysts 1, 2 and 3 for 1 mM loading inks.

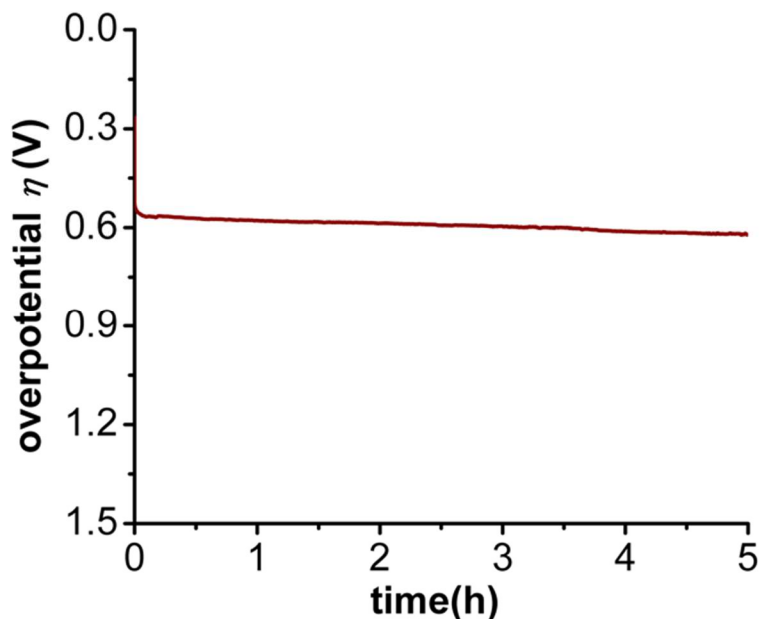
Catalyst	Time X (h)	Overpotential Y (V)	$\Delta X$ (h)	$\Delta Y$ (V)	$\Delta X/\Delta Y$ (mV/h)
1	0.03	0.79	4.96	0.06	-12.1
	4.99	0.73			
2	0.03	0.87	4.96	0.09	-18.1
	4.97	0.78			
3	0.03	0.88	4.96	0.07	-14.1
	4.99	0.81			



**Figure S31.** Stability tests of 1 for OER, under chronopotentiometry conditions at 10 mA for 5 h, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and 1.0 mM of catalyst as the working electrode. The experiment was performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.



**Figure S32.** Stability tests of **2** for OER, under chronopotentiometry conditions at 10 mA for 5 h, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and 1.0 mM of catalyst as the working electrode. The experiment was performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.



**Figure S33.** Stability tests of **3** for OER, under chronopotentiometry conditions at 10 mA for 5 h, obtained with 1 cm<sup>2</sup> carbon paper coated with ink containing Vulcan Carbon, Nafion and 1.0 mM of catalyst as the working electrode. The experiment was performed under N<sub>2</sub>, in 1.0 M KOH; Pt wire counter electrode, Hg/HgO reference electrode; 100 mV/s scan rate.

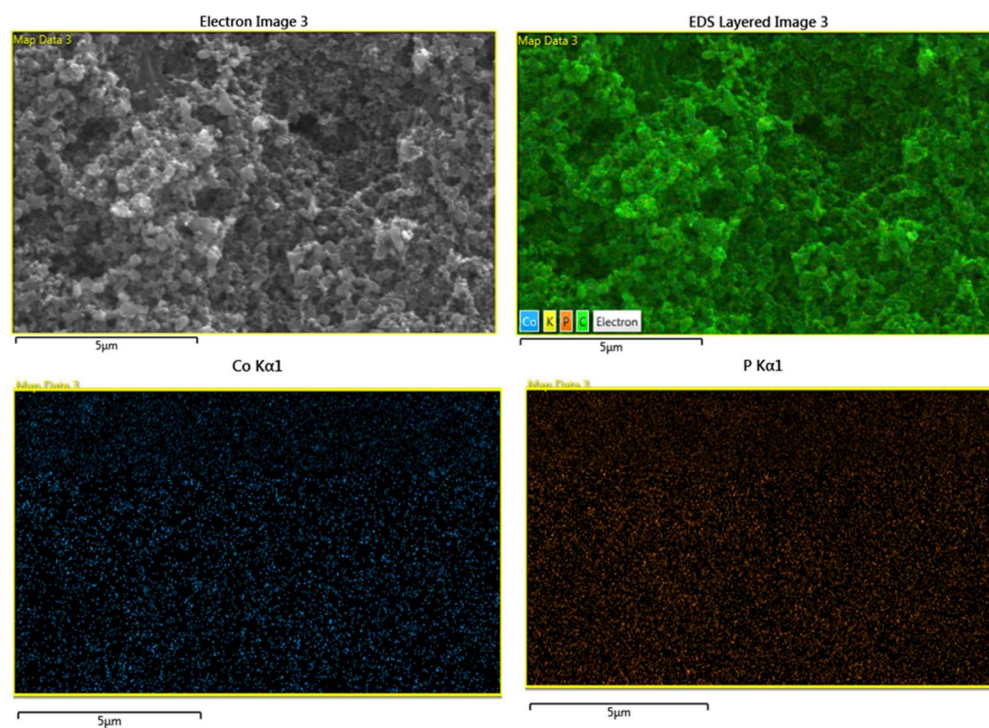
**Table S5.** Calculations for change of overpotential over time for stability tests after OER of catalysts **1**, **2** and **3** for 1 mM loading inks.

Catalyst	Time X (h)	Overpotential Y (V)	$\Delta X$ (h)	$\Delta Y$ (V)	$\Delta X/\Delta Y$ (mV/h)
<b>1</b>	0.03	0.62	4.96	0.03	6.04
	4.99	0.65			
<b>2</b>	0.03	0.61	4.96	0.09	18.1
	4.97	0.70			
<b>3</b>	0.03	0.55	4.96	0.07	14.1
	4.99	0.62			

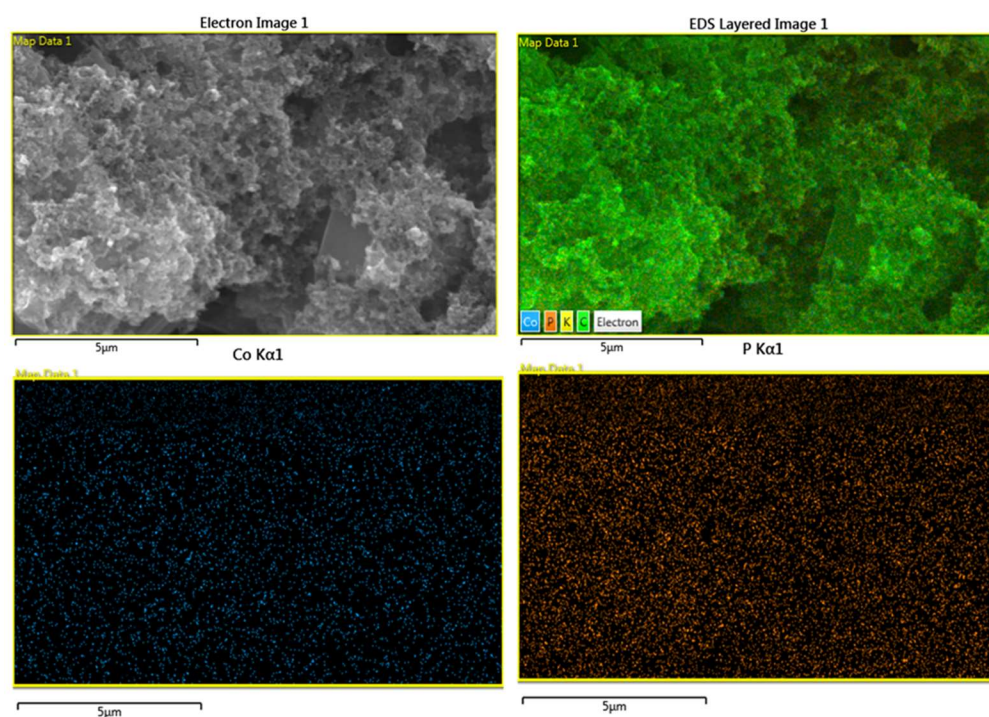
**Table S6.** TOF for **1**, **2** and **3** for 1 mM loading ink.

		<b>1</b>		<b>2</b>		<b>3</b>	
Conditions	Ink Conc	Co (ppm)	TOF (s <sup>-1</sup> )	Co (ppm)	TOF (s <sup>-1</sup> )	Co (ppm)	TOF (s <sup>-1</sup> )
As prepared for HER	1 mM	2.21	0.413	1.829	1.02	0.873	2.98
At -10 mA for 30 m	1 mM	2.19		1.850		0.561	
At -50 mA for 30 m	1 mM	1.96		1.322		0.511	
As prepared for OER	1 mM	2.26	0.169	2.023	0.301	0.798	1.11
At 10 mA for 30 m	1 mM	2.08		2.210		0.796	
At 50 mA for 30 m	1 mM	1.78		1.576		0.665	
As prepared for HER	3 mM	2.585	0.789	4.424	0.055	5.628	0.124
As prepared for OER	3 mM	2.393	0.236	3.703	0.095	5.603	0.065

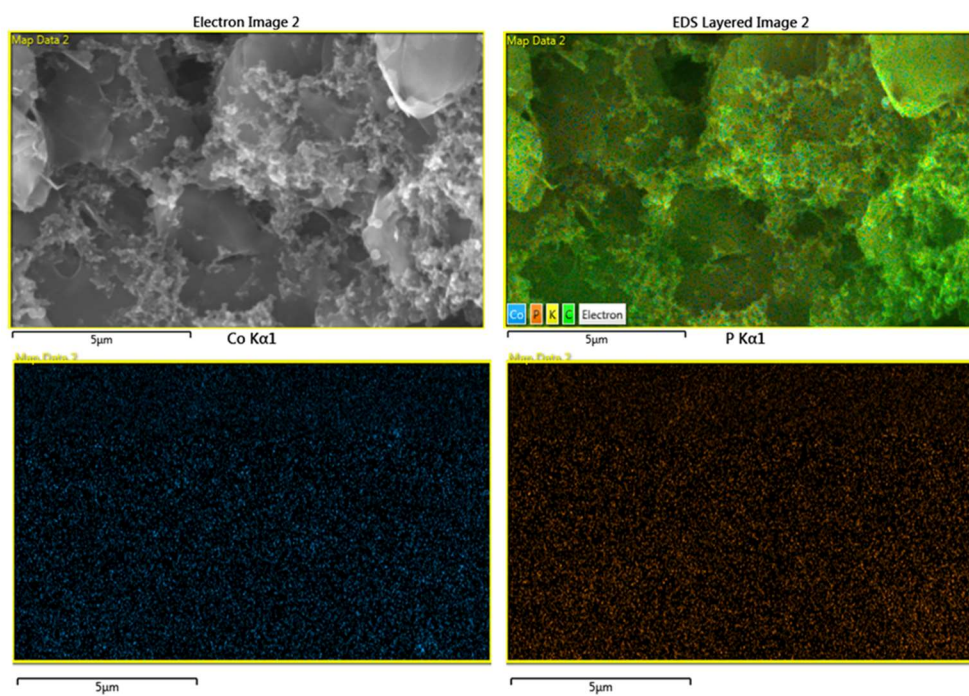
## Electron Microscopy



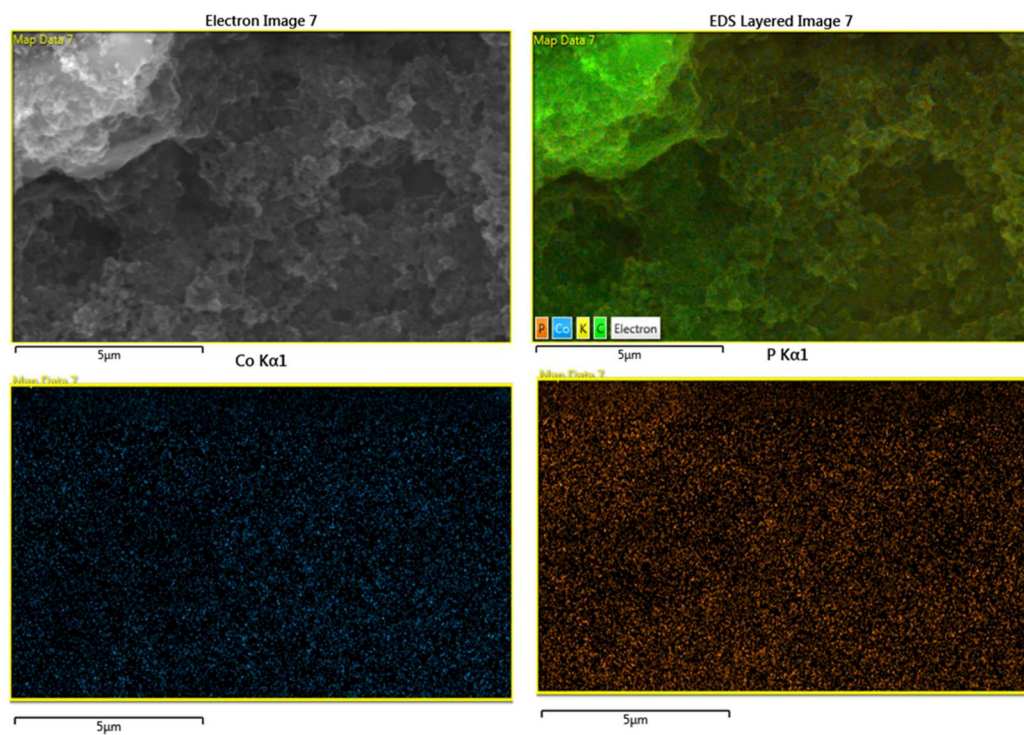
**Figure S34.** SEM-EDS images of **1** after HER. Ink prepared with 1 mM catalyst.



**Figure S35.** SEM-EDS images of **1** after HER, chronoamperometry at -10 mA for 30 m. Ink prepared with 1 mM catalyst.

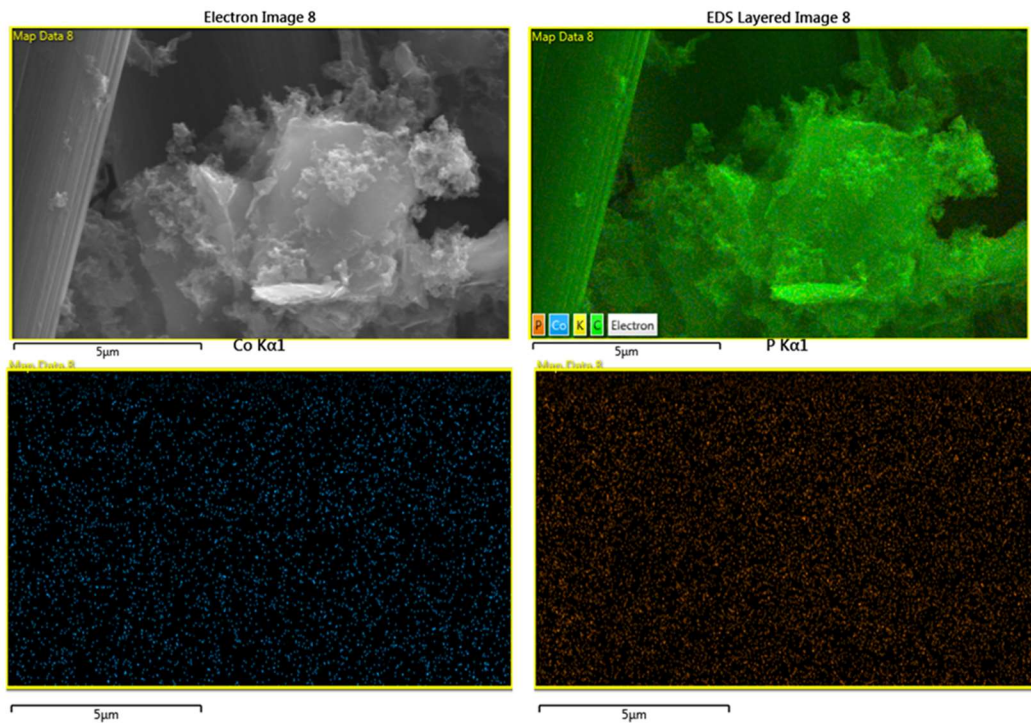


**Figure S36.** SEM-EDS images of **1** after HER, chronopotentiometry at  $-50$  mA for 30 m. Ink prepared with 1 mM catalyst.

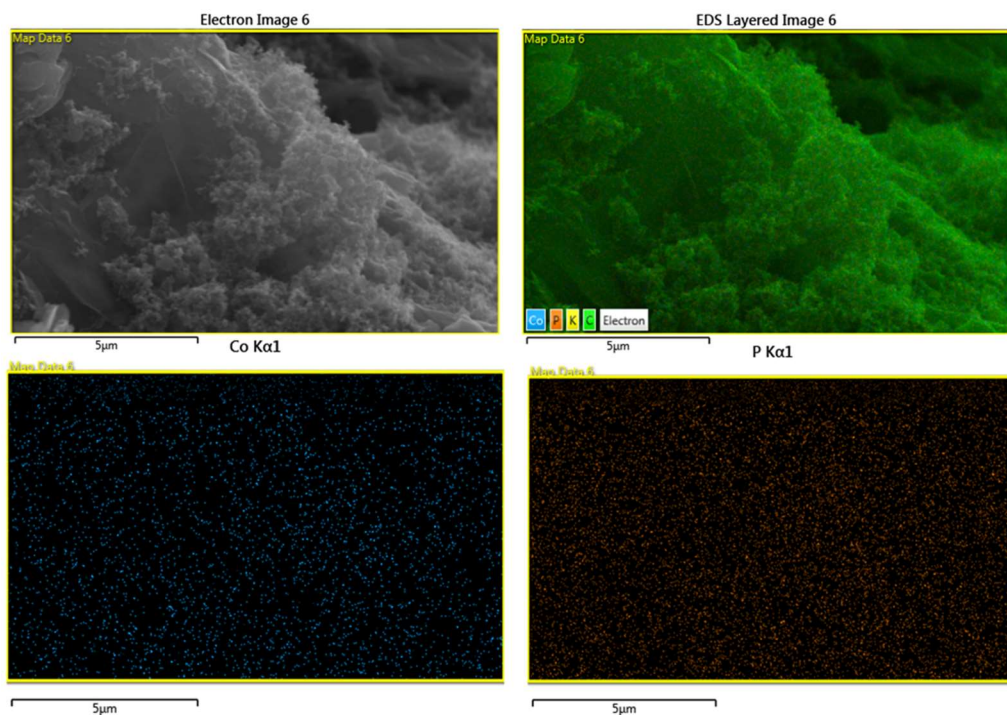


**Figure S37.** SEM-EDS images for **2** after HER. Ink prepared with 1 mM catalyst.

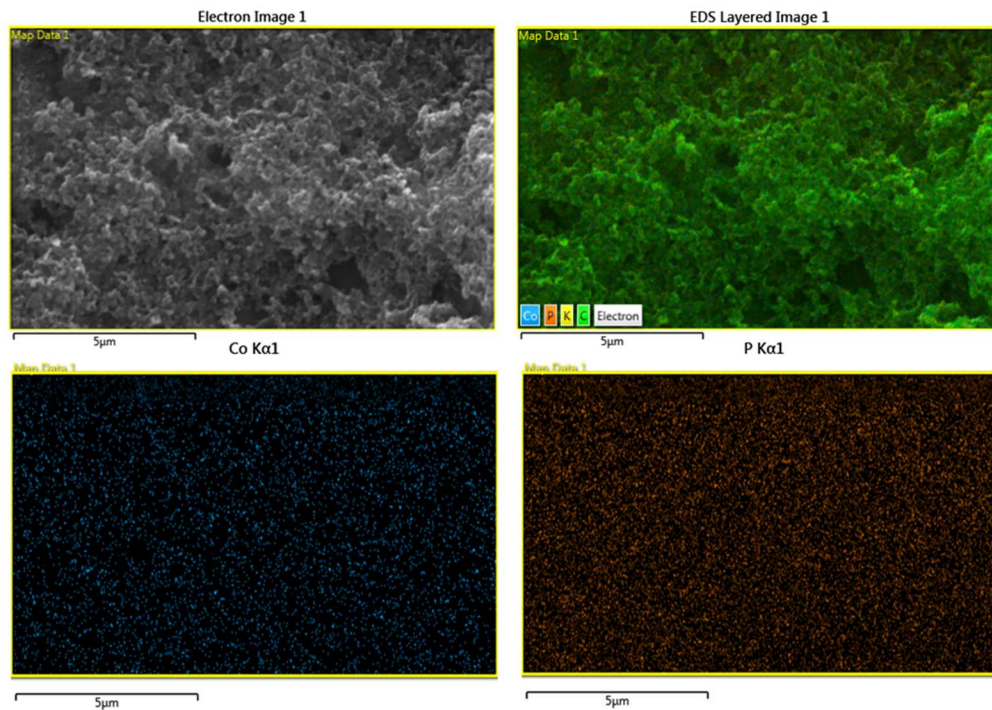




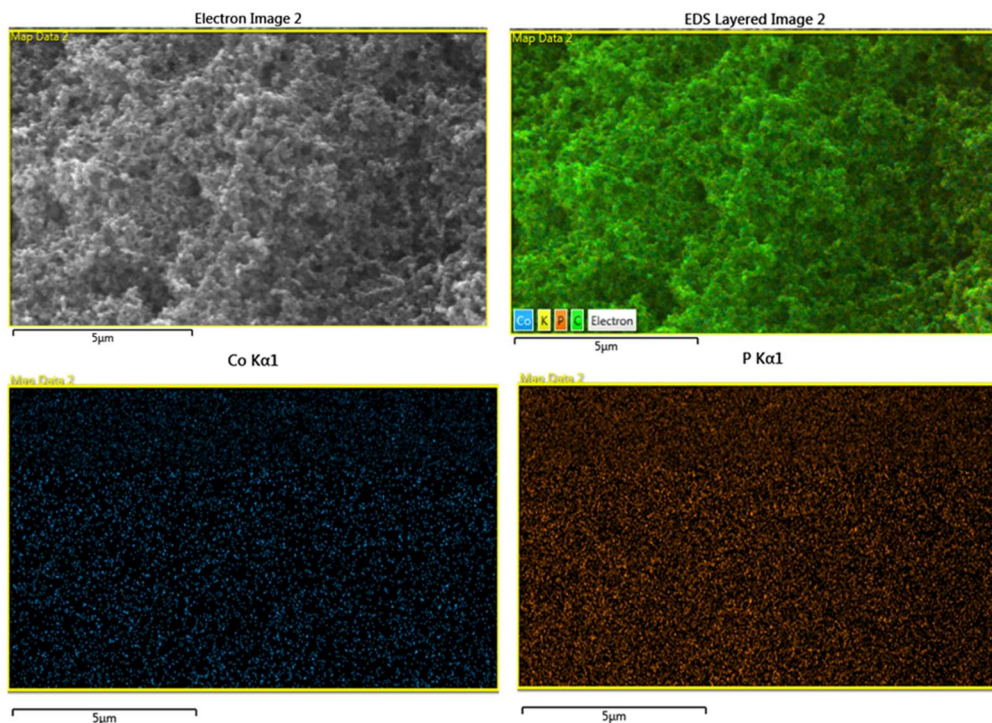
**Figure S38.** SEM-EDS images for **2** HER, chronopotentiometry at  $-10$  mA for 30mins. Ink prepared with 1 mM catalyst.



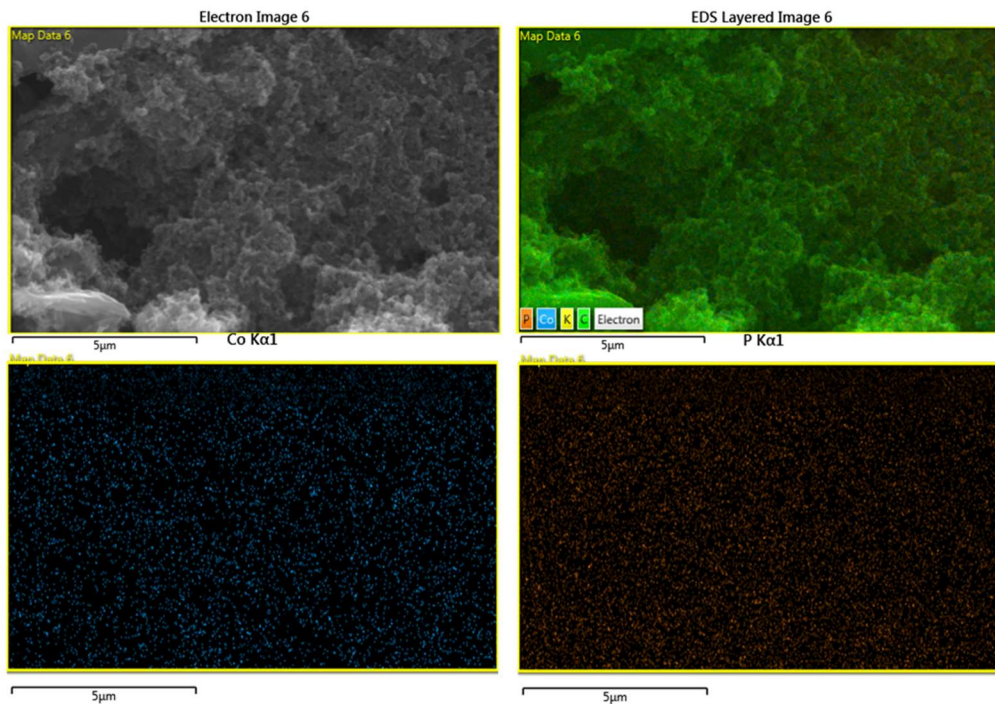
**Figure S39.** SEM-EDS images for **2** after HER, chronopotentiometry at  $-50$  mA for 30 m. Ink prepared with 1 mM catalyst.



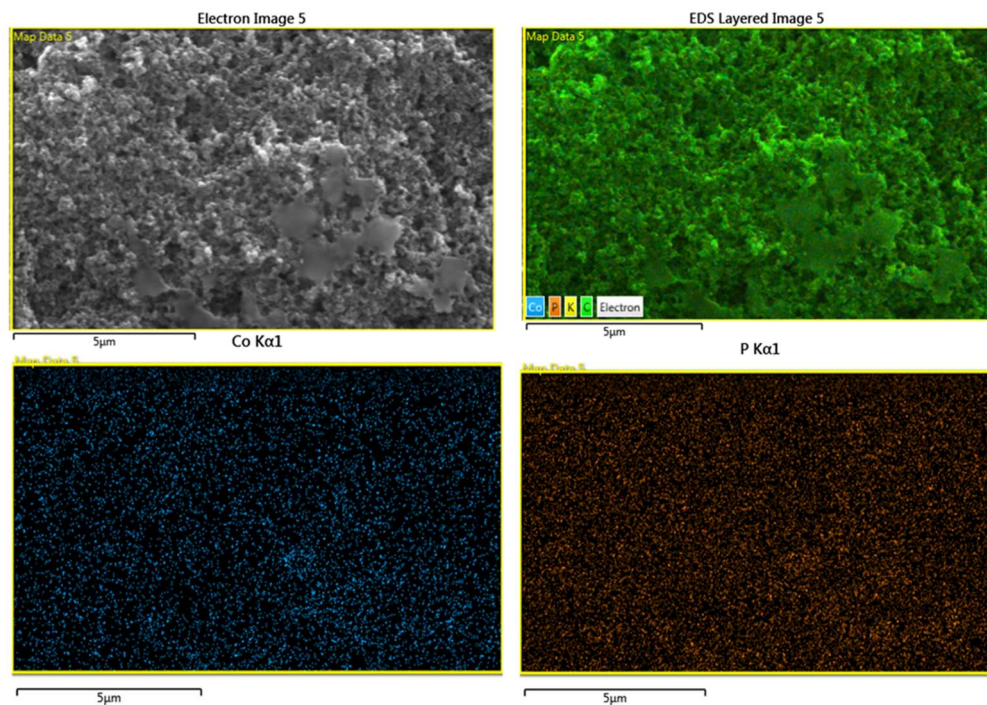
**Figure S40.** SEM-EDS images for **3** after HER. Ink prepared with 1 mM catalyst.



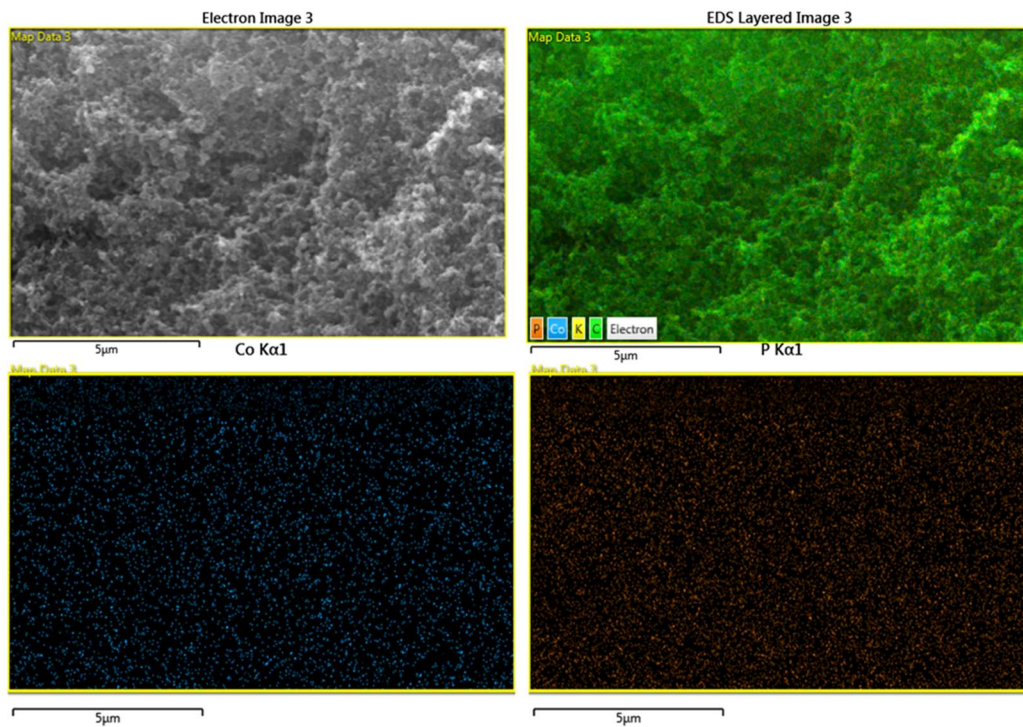
**Figure S41.** SEM-EDS images for **3** after HER, chronopotentiometry at  $-10$  mA for 30 m. Ink prepared with 1 mM catalyst.



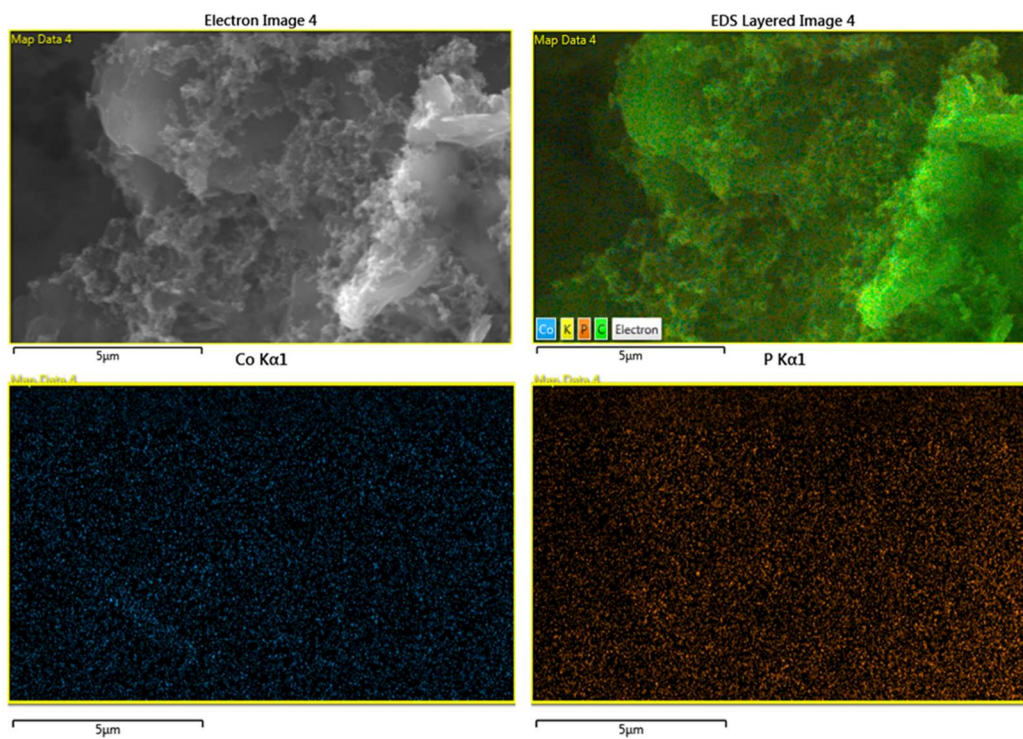
**Figure S42.** SEM-EDS images for **3** after HER, chronopotentiometry at  $-50$  mA for 30 m. Ink prepared with 1 mM catalyst.



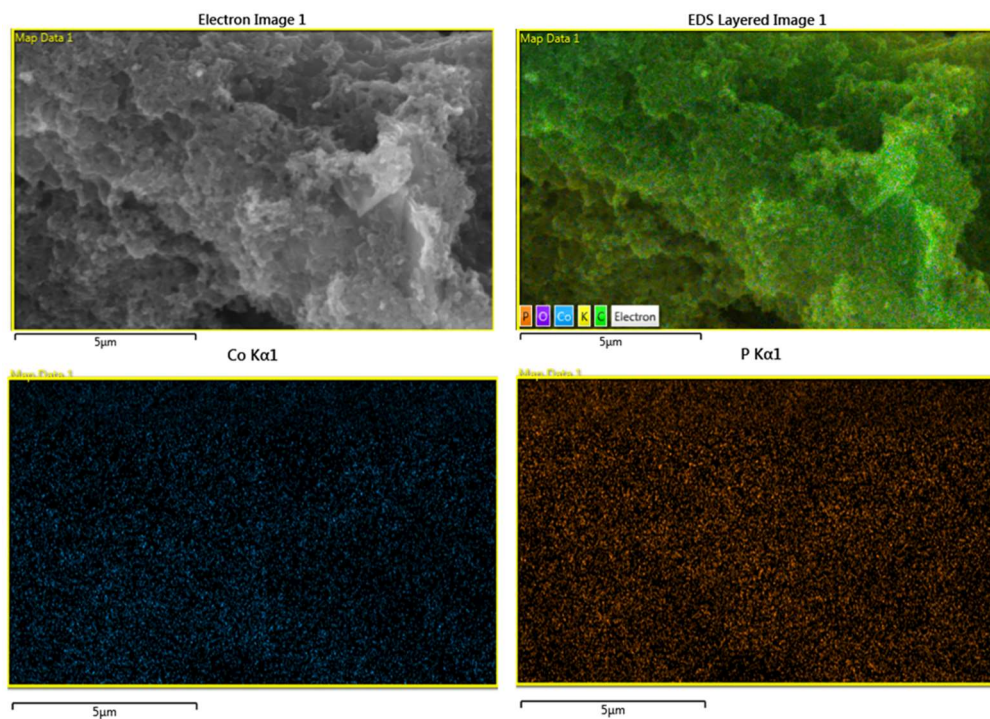
**Figure S43.** SEM-EDS images of **1** after OER. Ink prepared with 1 mM catalyst.



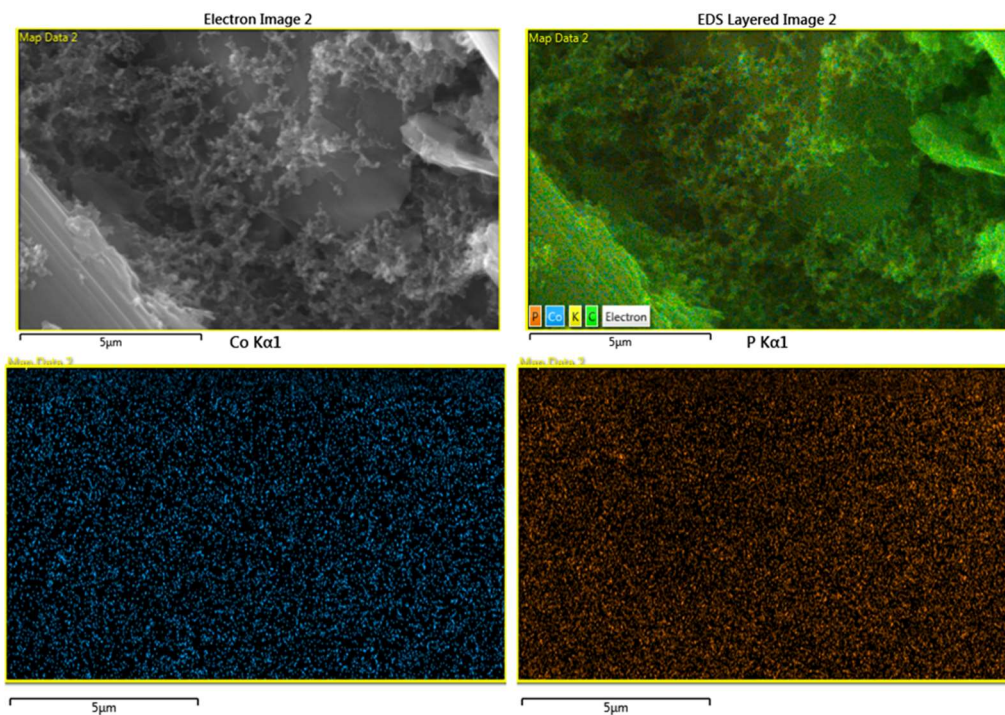
**Figure S44.** SEM-EDS images of **1** after OER, chronopotentiometry at 10 mA for 30 m. Ink prepared with 1 mM catalyst.



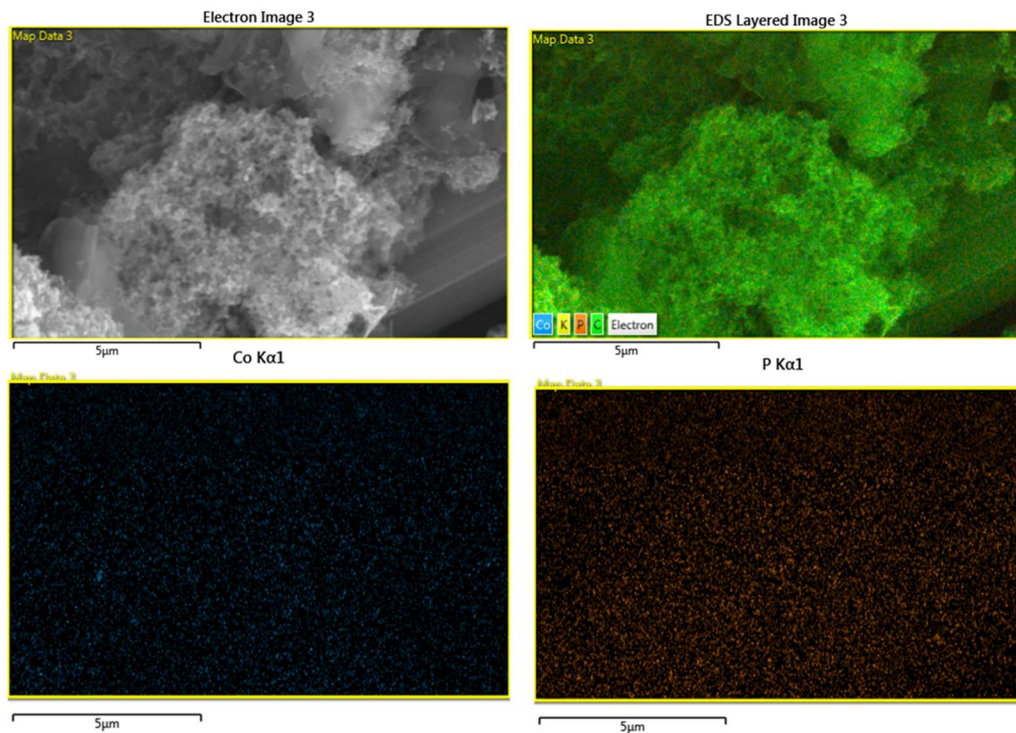
**Figure S45.** SEM-EDS images for **1** after OER, chronopotentiometry at 50 mA for 30 m. Ink prepared with 1 mM catalyst.



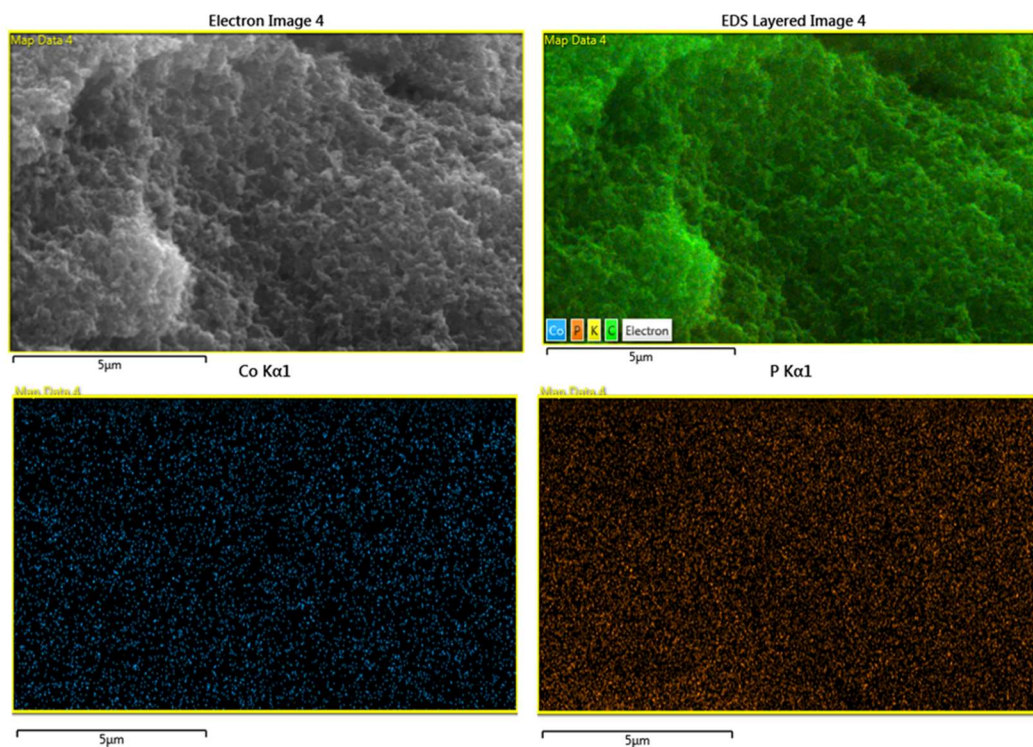
**Figure S46.** SEM-EDS images for **2** after OER. Ink prepared with 1 mM catalyst.



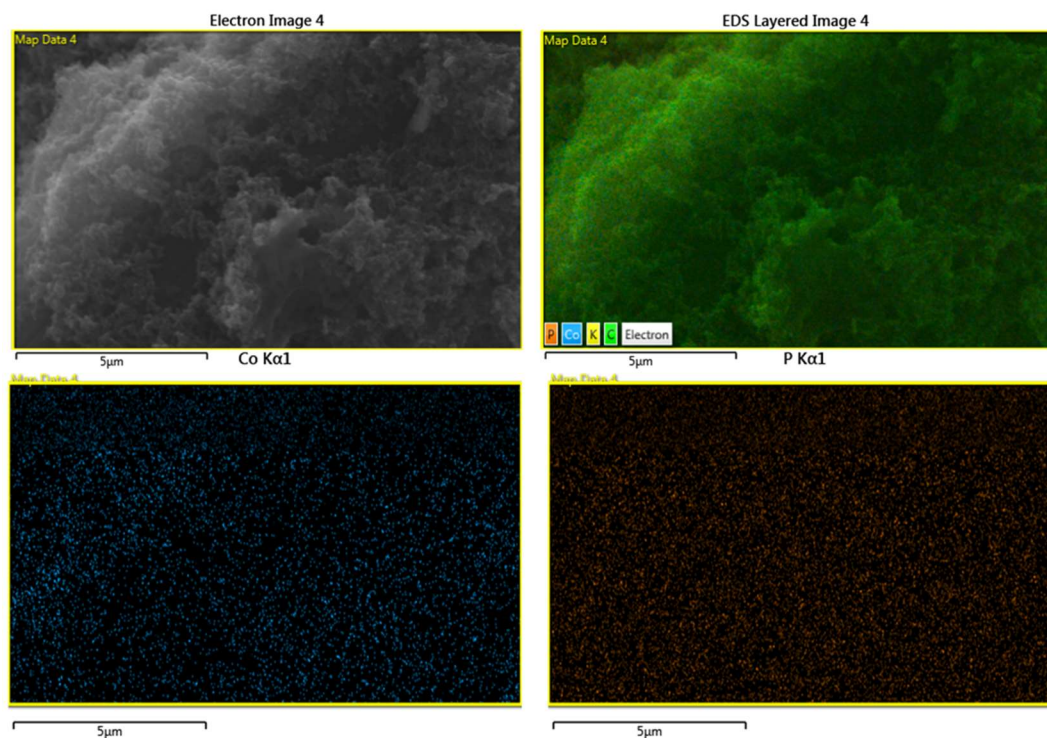
**Figure S47.** SEM-EDS images for **2** after OER, chronopotentiometry at 10 mA for 30 m. Ink prepared with 1 mM catalyst.



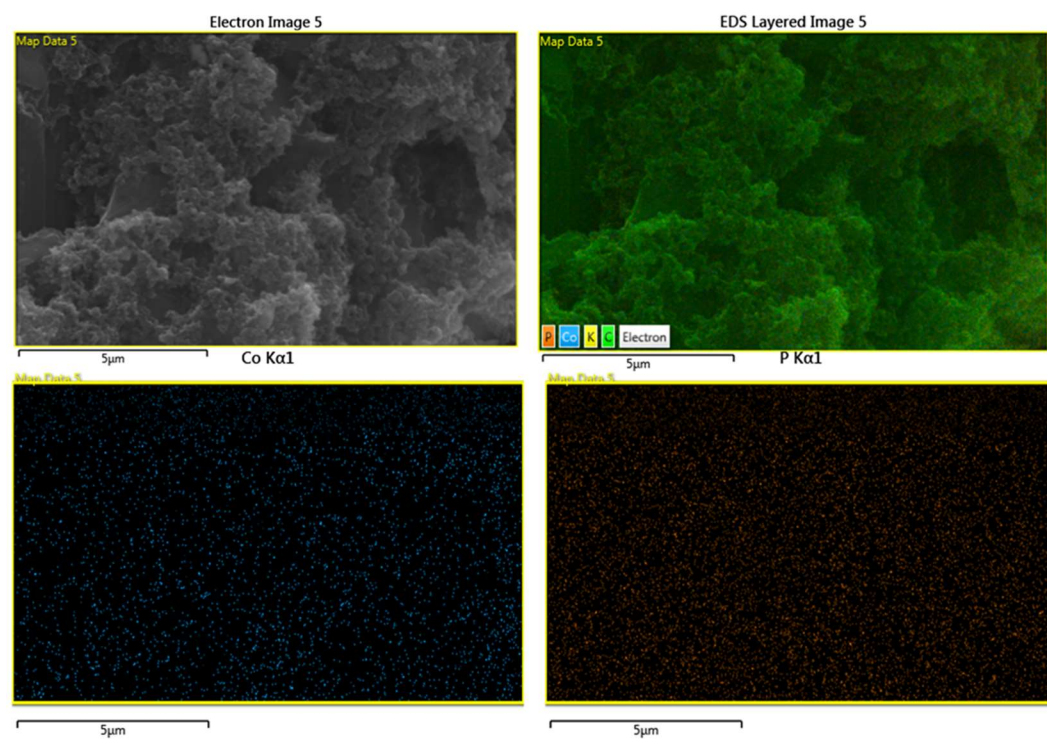
**Figure S48.** SEM-EDS images for **2** after OER, chronopotentiometry at 50 mA for 30 m. Ink prepared with 1 mM catalyst.



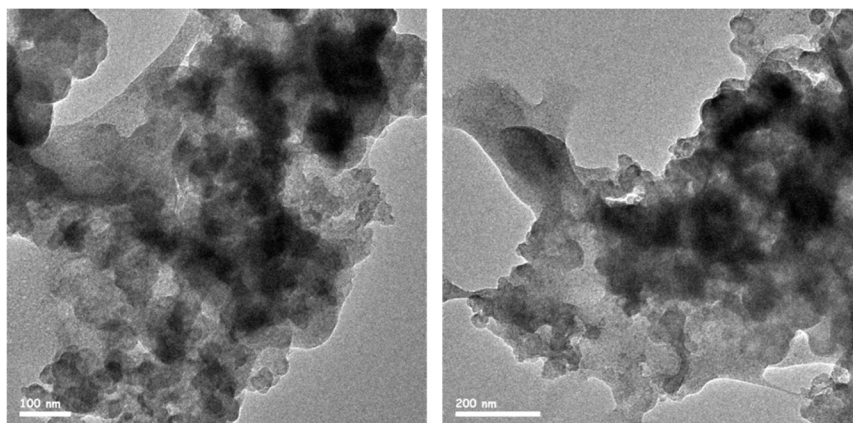
**Figure S49.** SEM-EDS images for **3** after OER. Ink prepared with 1 mM catalyst.



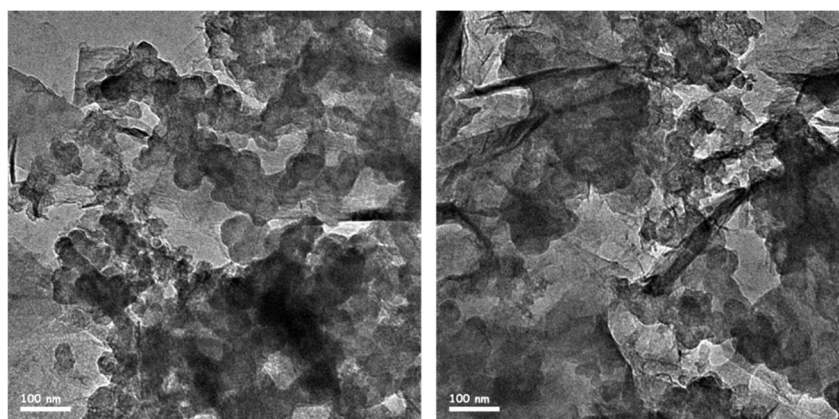
**Figure S50.** SEM-EDS images for **3** after OER, chronopotentiometry at 10 mA for 30 m. Ink prepared with 1 mM catalyst.



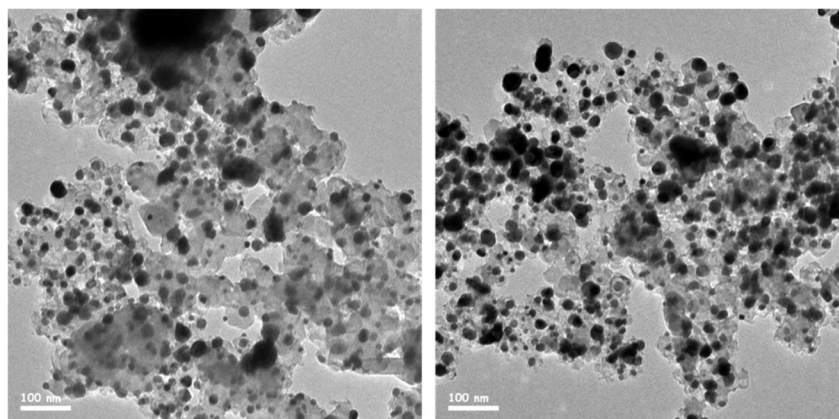
**Figure S51.** SEM-EDS images for **3** after OER, chronopotentiometry at 50 mA for 30 m. Ink prepared with 1 mM catalyst.



**Figure S52.** TEM images for **1** after HER, chronopotentiometry at  $-10$  mA for 30 m. Ink prepared with 1 mM catalyst.

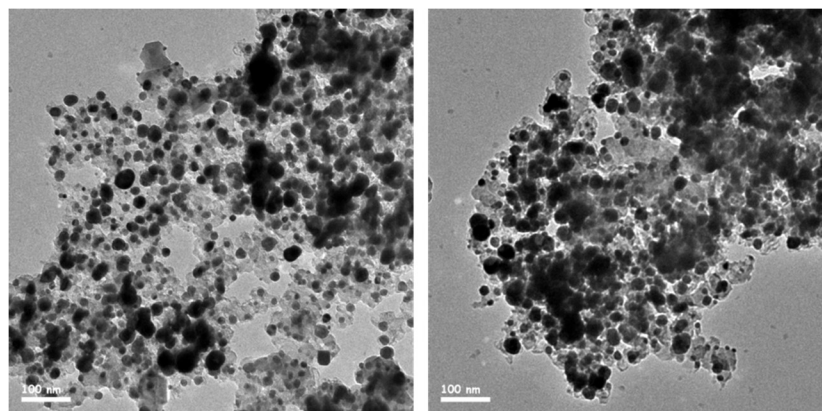


**Figure S53.** TEM images for **1** after HER chronopotentiometry at  $-50$  mA for 30 m. Ink prepared with 1 mM catalyst.

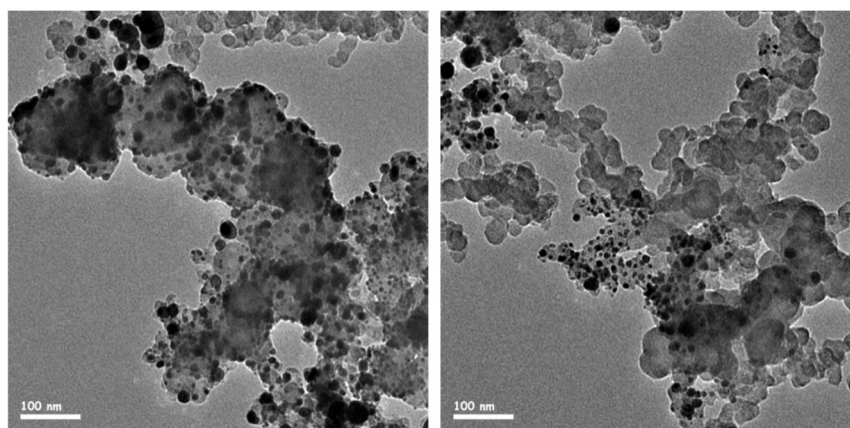


**Figure S54.** TEM images for **2** after HER chronopotentiometry at  $-10$  mA for 30 m. Ink prepared with 1 mM catalyst.

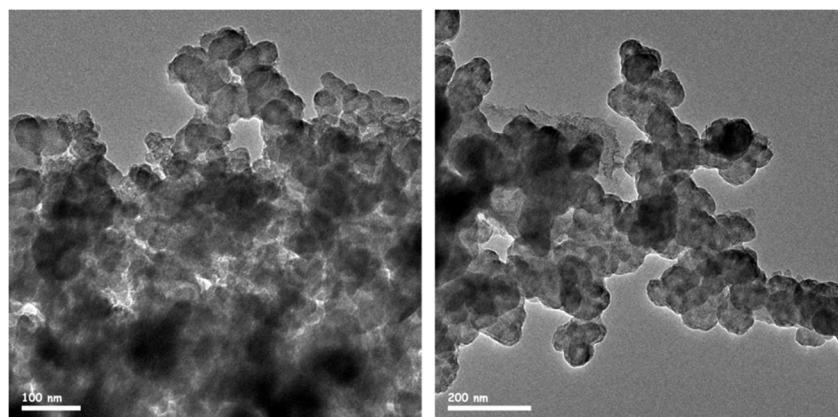




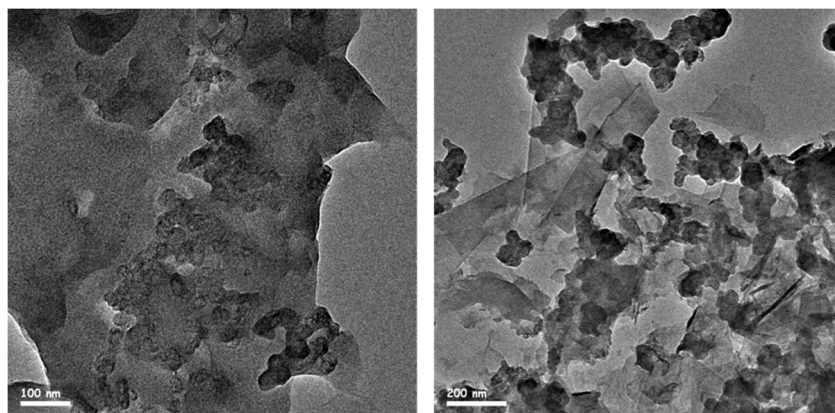
**Figure S55.** TEM images for **2** after HER chronopotentiometry at  $-50$  mA for 30 m. Ink prepared with 1 mM catalyst.



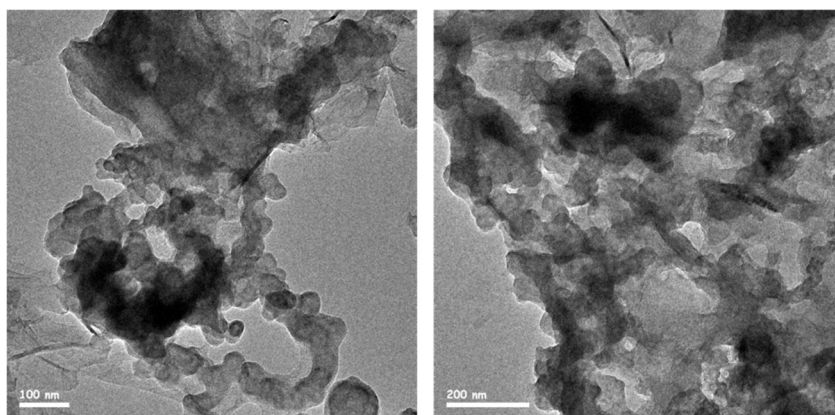
**Figure S56.** TEM images for **3** after HER chronopotentiometry at  $-10$  mA for 30 m. Ink prepared with 1 mM catalyst.



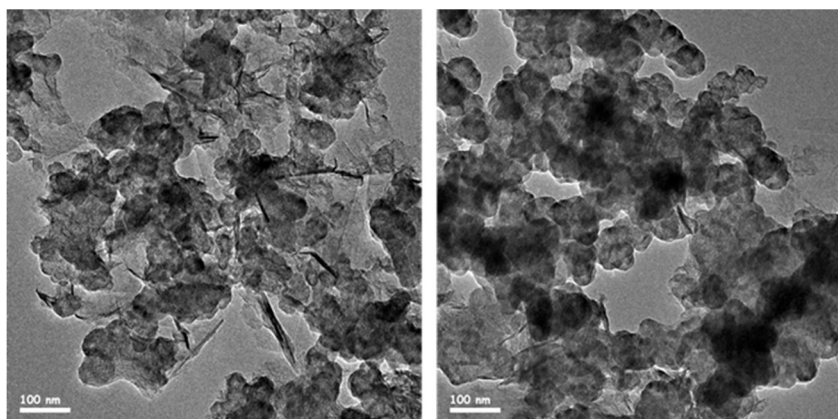
**Figure S57.** TEM images for **3** after HER chronopotentiometry at  $-50$  mA for 30 m. Ink prepared with 1 mM catalyst.



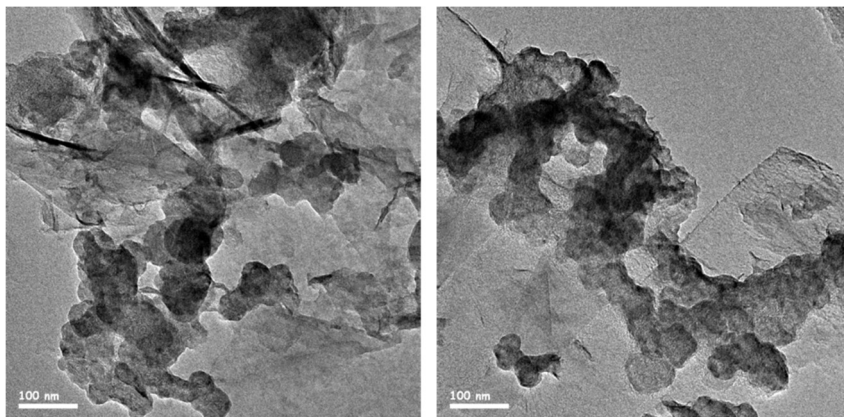
**Figure S58.** TEM images for **1** after OER chronopotentiometry at 10 mA for 30 m. Ink prepared with 1 mM catalyst.



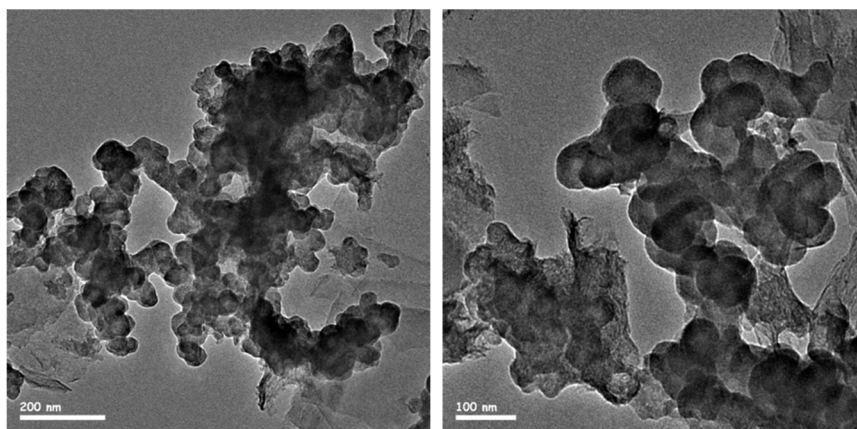
**Figure S59.** TEM images for **1** after OER chronopotentiometry at 50 mA for 30 m. Ink prepared with 1 mM catalyst.



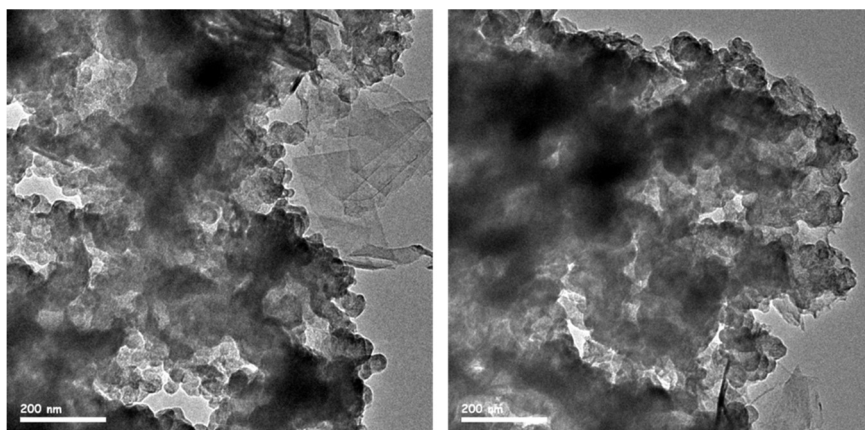
**Figure S60.** TEM images for **2** after OER chronopotentiometry at 10 mA for 30 m. Ink prepared with 1 mM catalyst.



**Figure S61.** TEM images for **2** after OER chronopotentiometry at 50 mA for 30 m. Ink prepared with 1 mM catalyst.



**Figure S62.** TEM images for **3** after OER chronopotentiometry at 10 mA for 30 m. Ink prepared with 1 mM catalyst.



**Figure S63.** TEM images for **3** after OER chronopotentiometry at 50 mA for 30 m. Ink prepared with 1 mM catalyst.

## **References**

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