

Electronic Supplementary Information (ESI)

Catalytic nickel and nickel-copper alloy hollow-fiber membranes for remediation of organic pollutants by electrocatalysis

Authors:

Francois-Marie Allioux^{1*}, Oana David², Andrea Merenda¹, James Maina¹, Miren Etxeberria Benavides², Lingxue Kong¹, Alfredo Pacheco Tanaka², Ludovic F. Dumée^{1*}

Affiliations:

¹ Deakin University, Geelong, Institute for Frontier Materials, Victoria, 3216, Australia

² TECNALIA, Energy and Environment Division, Mikeletegi Pasealekua 2, 20009, San Sebastian-Donostia, Spain

Corresponding authors*

f.allioux@deakin.research.edu.au ; Ludovic.dumee@deakin.edu.au

Spinning conditions

Table S1. Spinning conditions of the Ni and NiCu HFs.

| Sample | Dope flow rate (mL.h ⁻¹) | Air gap (cm) | Bore flow rate (mL.h ⁻¹) | Bore composition |
|---------|---|-----------------|---|------------------|
| Ni HF | 300 | 1.5 | 150 | Water |
| NiCu HF | 300 | 1.5 | 150 | Water |

Table S2. Size distribution of the Ni and NiCu metal powder.

| Metal particles | Equivalent spherical diameter in DI water (μm) | | | Equivalent spherical diameter in IP (μm) | | |
|-----------------|--|------------|------------|--|------------|------------|
| | d0.1 | d0.5 | d0.9 | d0.1 | d0.5 | d0.9 |
| Ni | 7.4 ± 0.2 | 19.6 ± 0.2 | 36.6 ± 0.7 | 7.1 ± 0.1 | 18.9 ± 0.1 | 36.6 ± 0.2 |
| NiCu | 12.5 ± 0.3 | 31.2 ± 0.5 | 56.3 ± 0.2 | 14.8 ± 0.3 | 32.6 ± 0.9 | 58.4 ± 0.8 |

Table S3. Average absolute density and relative density of the metal powders determined versus average bulk density of Ni and NiCu Monel 400 alloy.

| Metal powder | Average absolute density (g.cm ⁻³) | Relative density (%) |
|--------------|---|-------------------------|
| Ni | 5.71 | 35.86 |
| NiCu | 4.25 | 51.71 |

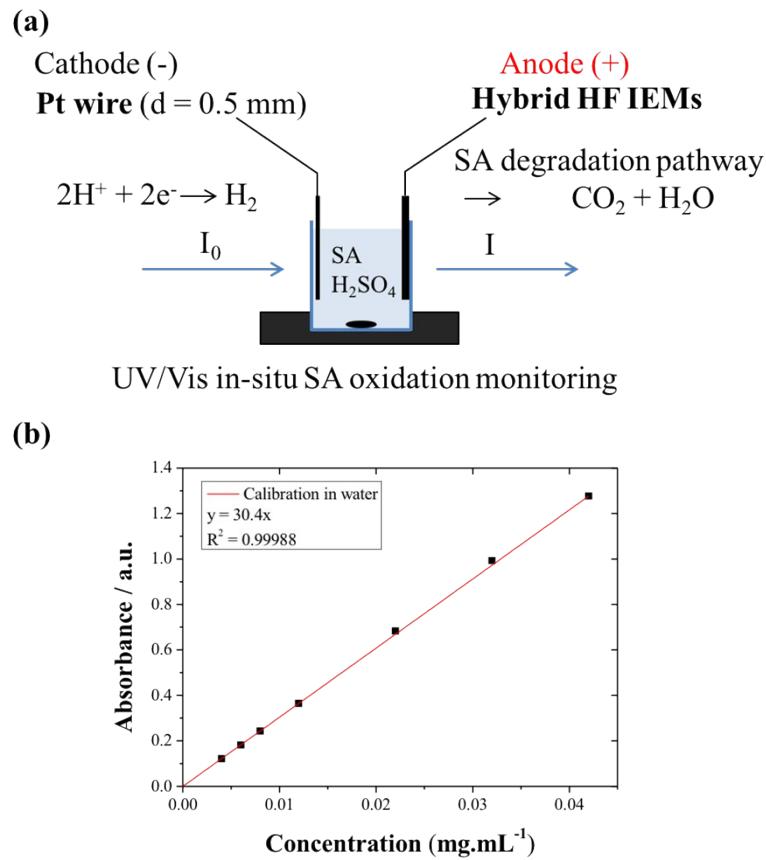


Fig.S1 (a): UV/vis experimental set-up for the in-situ monitoring of SA electrochemical oxidation with possible electrode reactions, SA degradation pathway.¹ (b): UV/vis calibration curve of SA in DI water.

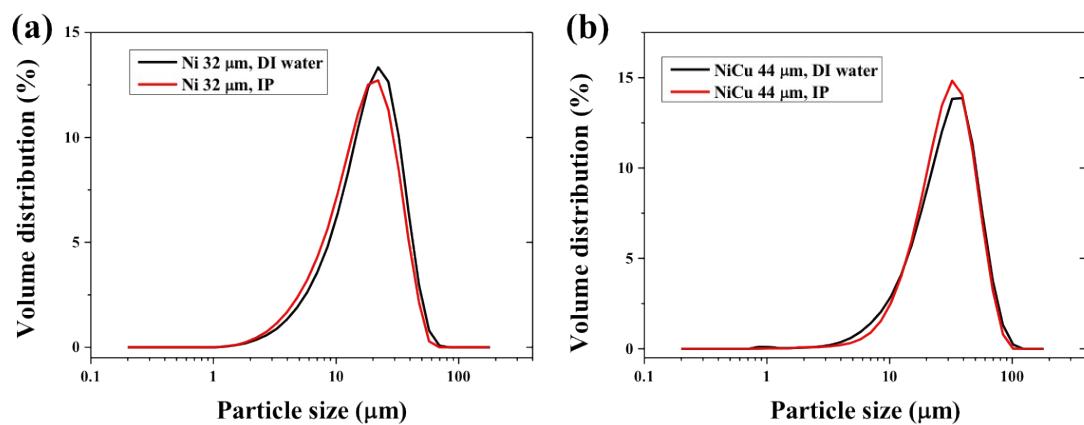


Fig. S2 Size measurement of (a): Ni powder and (b): NiCu powder in DI water and IP.

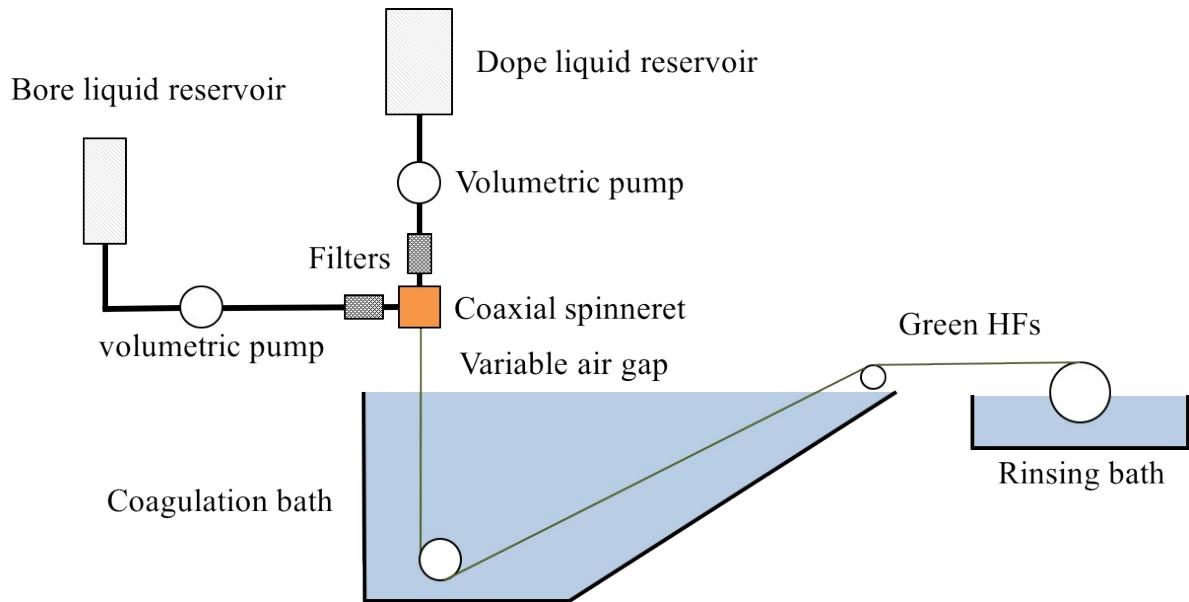


Fig. S3 Schematic representation of the dry-wet spinning set-up.

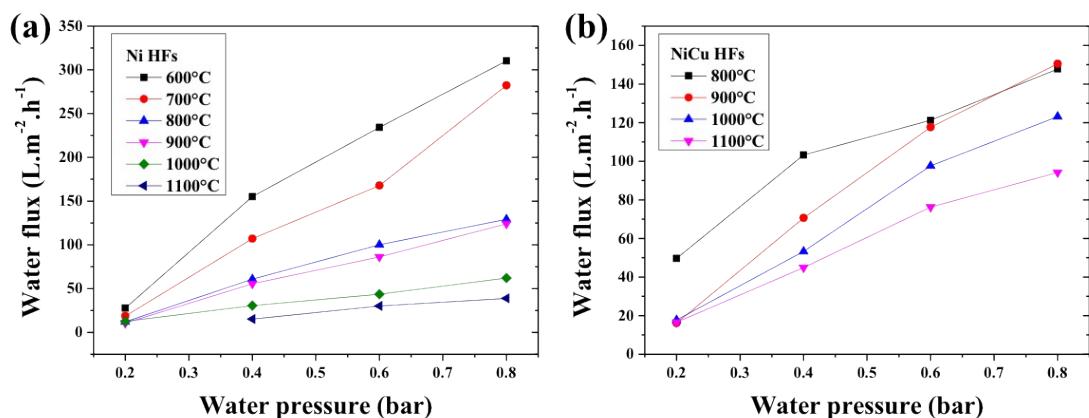


Fig. S4 Water fluxes as a function of the water pressure of (a): Ni HF and (b): NiCu HF.

XPS analysis

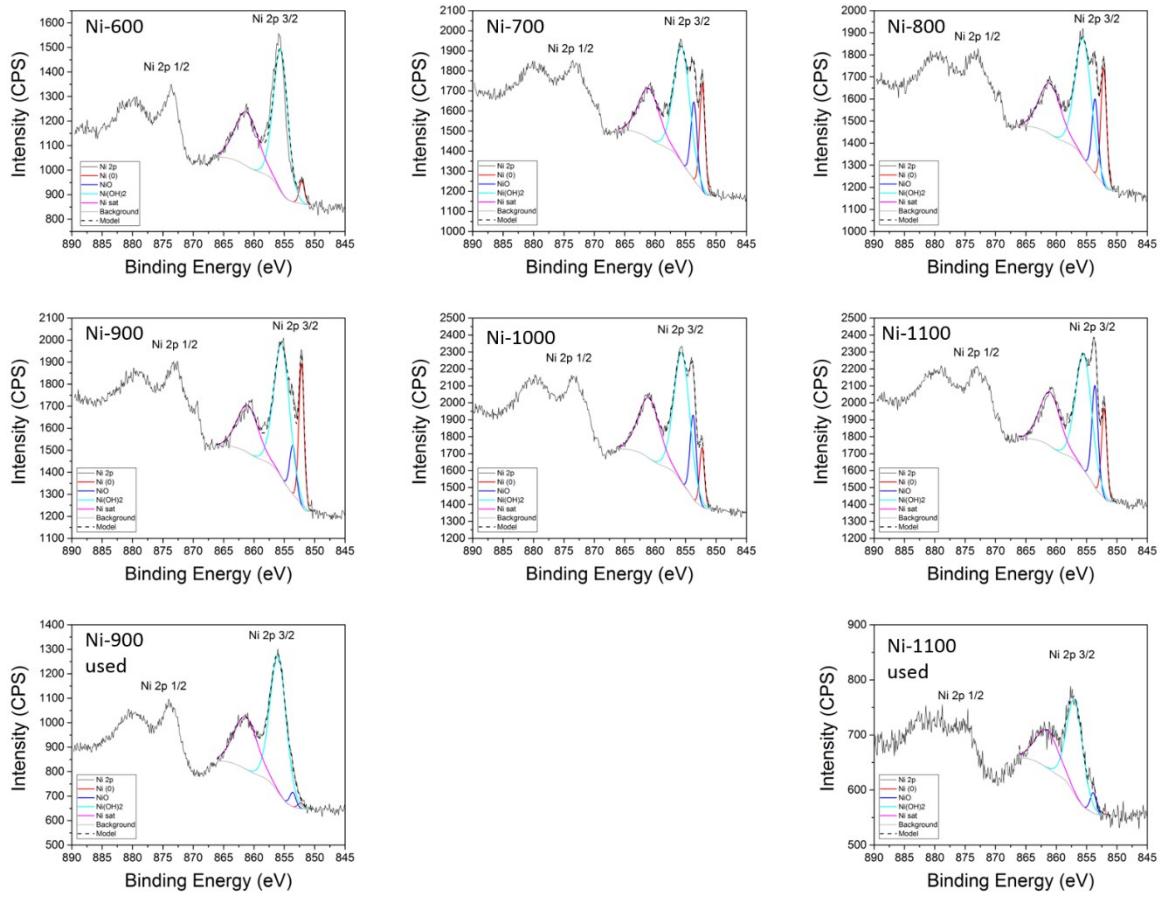


Fig. S5 XPS HR spectra of Ni HF at different heat treatment temperature

| Chemical State | Position (eV) | FWH M (eV) | Ni 600 (%) | Ni 700 (%) | Ni 800 (%) | Ni 900 (%) | Ni 1000 (%) | Ni 1100 (%) | Ni 900- Used (%) | Ni 1100- Used (%) |
|-----------------|---------------|------------|------------|------------|------------|------------|-------------|-------------|------------------|-------------------|
| Ni (0) | 852.2 | 1 | 3.58 | 14.44 | 16.06 | 17.99 | 6.88 | 11.7 | 0.95 | 0.28 |
| NiO | 853.6 | 1.2 | 0 | 12.26 | 11.3 | 7.27 | 12.47 | 15.51 | 2.51 | 5.02 |
| Ni(OH)2 | 855.6 | 3 | 59.54 | 47.08 | 46.31 | 50.58 | 49.48 | 45.46 | 62.1 | 60.09 |
| Ni sat | 861.2 | 4 | 36.88 | 26.23 | 26.33 | 24.16 | 31.17 | 27.33 | 34.43 | 34.61 |
| -- | | | -- | -- | -- | -- | -- | -- | -- | -- |
| Ni(OH)2: | | | n/a | 3.84 | 4.1 | 6.96 | 3.96 | 2.93 | 24.74 | 11.97 |
| NiO | | | | | | | | | | |

Table S4. Ni and Ni oxides species evaluated from the Ni 2p 3/2 HR spectra of Ni HF

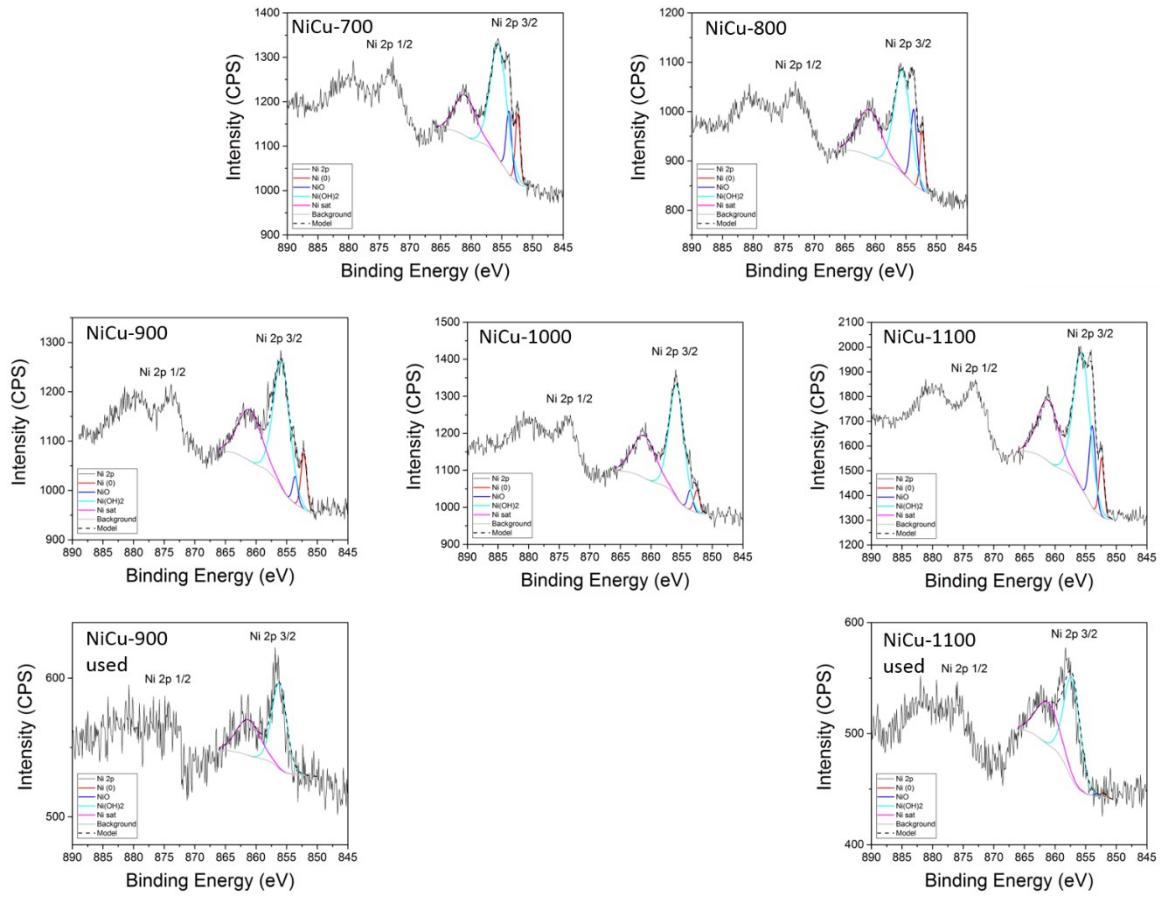


Fig. S6 XPS HR spectra of Ni 2p of NiCu HF at different heat treatment temperature.

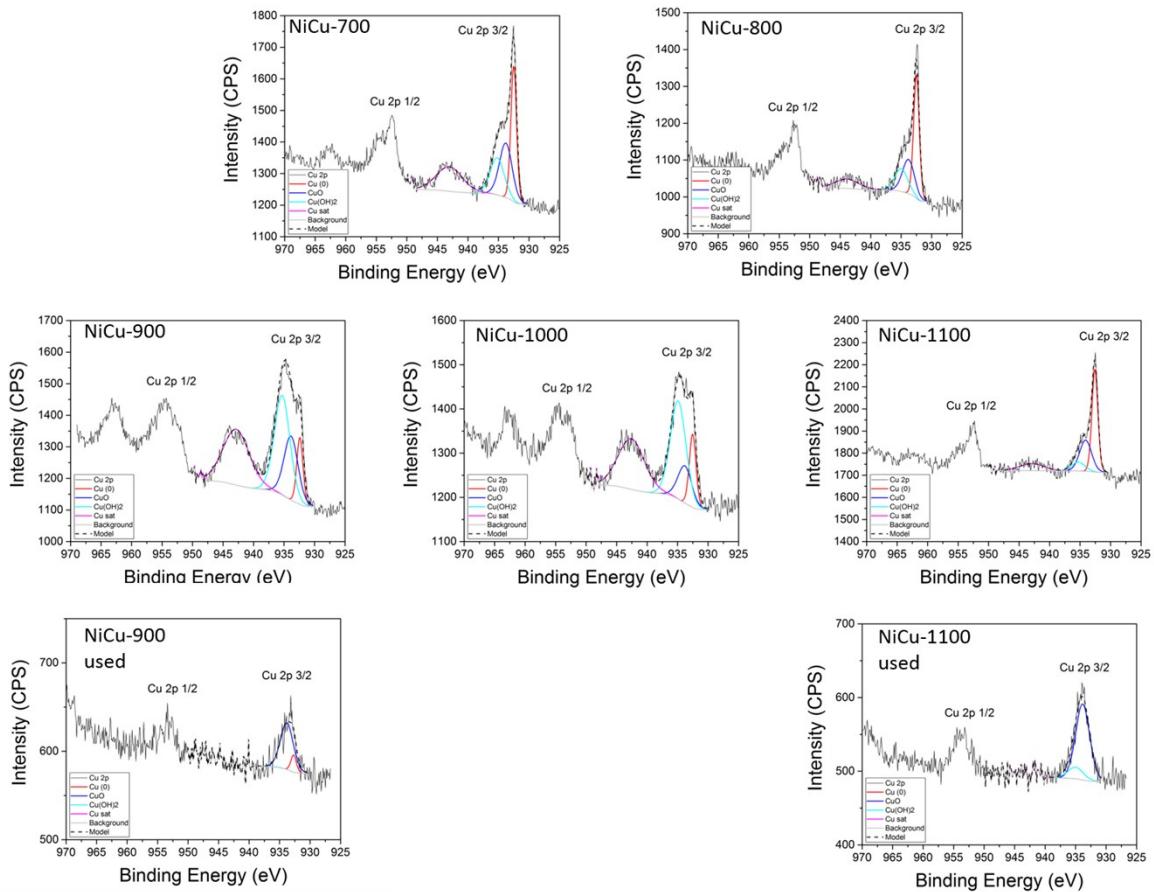


Fig. S7 XPS HR spectra of Cu 2p of NiCu HF at different heat treatment temperature.

| Sample ID | Ni/Cu ratio |
|-----------------------|-------------|
| NiCu-700 | 2.3 |
| NiCu-800 | 3.0 |
| NiCu-900 | 0.7 |
| NiCu-900 used | 4.7 |
| NiCu-1000 | 1.3 |
| NiCu-1100 | 5.3 |
| NiCu-1100 used | 3.4 |

Table S5 Variation of Ni/Cu ratio evaluated by XPS analysis across the series of different heat treatment.

| Chemical State | Position (eV) | FWHM (eV) | NiCu 700 (%) | NiCu 800 (%) | NiCu 900 (%) | NiCu 1000 (%) | NiCu 1100 (%) | NiCu 900-Used (%) | NiCu 1100-Used (%) |
|-----------------|---------------|-----------|--------------|--------------|--------------|---------------|---------------|-------------------|--------------------|
| Ni (0) | 852.4 | 1 | 9.82 | 7.99 | 8.62 | 4.51 | 6.88 | 0.05 | 0.96 |
| NiO | 853.8 | 1.1 | 10.29 | 13.47 | 3.84 | 3.65 | 11.9 | 0 | 0.09 |
| Ni(OH)2 | 855.8 | 3 | 54.66 | 47.41 | 55.27 | 57.56 | 51.46 | 59.93 | 61.9 |
| Ni sat | 861.1 | 4.3 | 25.23 | 31.12 | 32.27 | 34.28 | 29.76 | 40.02 | 37.05 |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Ni(OH)2: | -- | -- | 5.31 | 3.51 | 14.39 | 15.76 | 4.32 | n/a | n/a-- |
| NiO | | | | | | | | | |

Table S6 Ni and Ni oxides species evaluated from the Ni 2p 3/2 HR spectra of Ni HF

| Chemical State | Position (eV) | FWHM (eV) | Ni 700 (%) | Ni 800 (%) | Ni 900 (%) | Ni 1000 (%) | Ni 1100 (%) | Ni 900-Used (%) | Ni 1100-Used (%) |
|-------------------------|---------------|-----------|------------|------------|------------|-------------|-------------|-----------------|------------------|
| Cu (0) | 932.5 | 1.1 | 29.46 | 43.2 | 9.58 | 12.72 | 48.41 | 13.5 | 0 |
| CuO | 933.8 | 2.3 | 26.52 | 25.04 | 20.64 | 13.4 | 29.31 | 85.97 | 84.22 |
| Cu(OH) 2 | 935.1 | 2.5 | 19.67 | 18.08 | 35.73 | 39.35 | 9.16 | 0.53 | 14.28 |
| Cu sat | 943.85 | 4.5 | 24.35 | 13.67 | 34.05 | 34.53 | 13.12 | 0 | 1.5 |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Cu(OH) 2:CuO | -- | -- | 0.7417 | 0.72204 | 1.7311 | 2.93657 | 0.31252 | 0.00616 | 0.16956 |

Table S7 Cu and Cu oxides evaluated from Cu 2p 3/2 spectra of NiCu HF

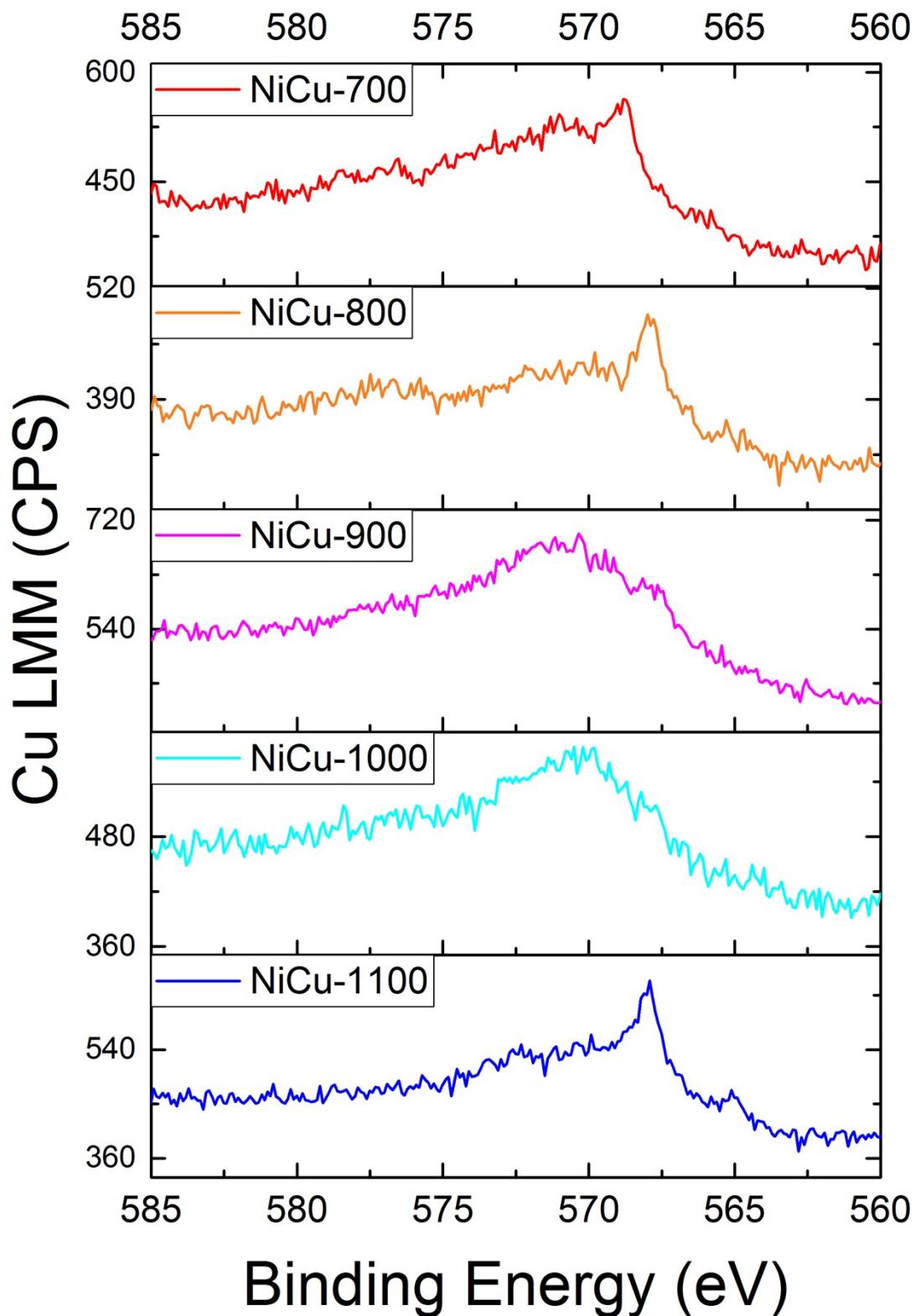


Fig. S8 XPS investigation of Cu LMM transition for NiCu HF at different heat treatment temperature

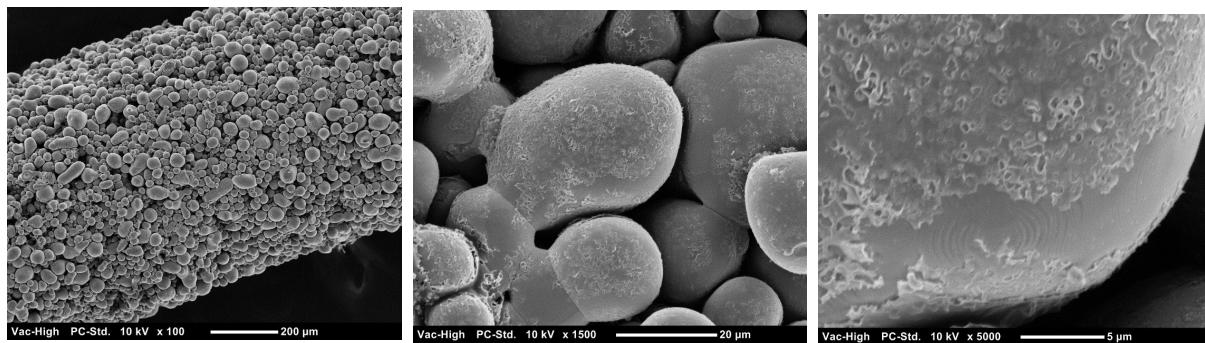


Fig. S9 SEM of the 900°C annealed NiCu HF sample post electrocatalysis. Mild oxidation of the surface of the particles is visible on the right-hand image with pittings smaller than 100 nm

Table S8. Weight concentrations of the elements across the Ni HF samples calculated from the EDX elemental analysis.

| Samples | Ni wt% | C wt% | O wt% |
|--------------|------------|------------|-----------|
| Ni HF 600°C | 81.3 ± 0.8 | 12.5 ± 0.9 | 1.6 ± 0.2 |
| Ni HF 700°C | 72.5 ± 0.4 | 25.0 ± 0.4 | 1.3 ± 0.1 |
| Ni HF 800°C | 81.5 ± 0.8 | 14.7 ± 0.8 | |
| Ni HF 900°C | 75.6 ± 0.2 | 20.5 ± 0.2 | 1.8 ± 0.1 |
| Ni HF 1000°C | 78.3 ± 0.2 | 18.7 ± 0.2 | 1.2 ± 0.1 |
| Ni HF 1100°C | 83.4 ± 0.2 | 15.4 ± 0.2 | 1.1 ± 0.1 |

Table S9. Weight concentrations of the elements across the NiCu HF samples calculated from the EDX elemental analysis.

| Samples | Ni wt% | Cu wt% | C wt% | O wt% |
|----------------|------------|------------|------------|-----------|
| NiCu HF 700°C | 56.0 ± 0.3 | 32.5 ± 0.3 | 6.3 ± 0.3 | 1.2 ± 0.1 |
| NiCu HF 800°C | 56.3 ± 0.3 | 31.6 ± 0.3 | 8.4 ± 0.4 | |
| NiCu HF 900°C | 56.5 ± 0.4 | 28.3 ± 0.3 | 10.0 ± 0.4 | 1.6 ± 0.1 |
| NiCu HF 1000°C | 26.3 ± 0.3 | 28.4 ± 0.3 | 10.9 ± 0.6 | |
| NiCu HF 1100°C | 37.0 ± 0.3 | 47.7 ± 0.3 | 9.0 ± 0.4 | |