Supporting Information

Fe-Ni porphyrin / mesoporous titania thin film electrodes: a bioinspired nanoarchitecture for photoelectrocatalysis

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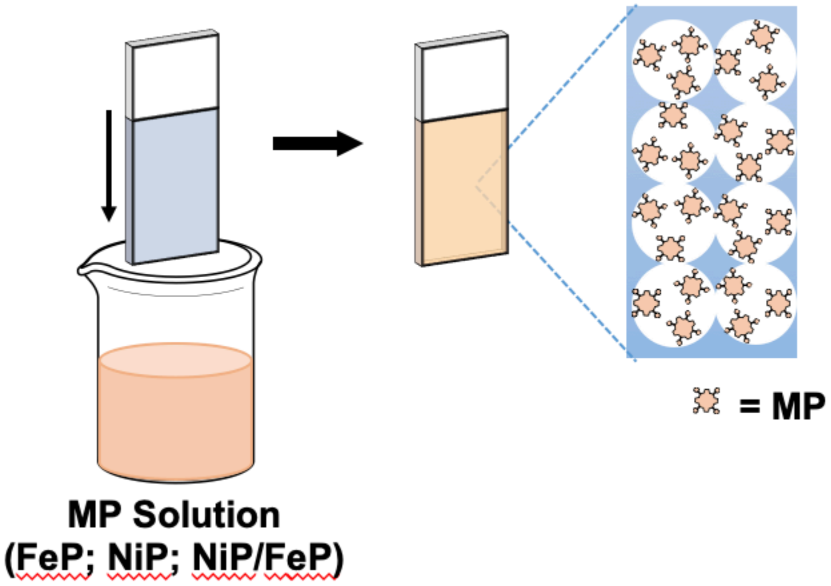

Scheme S1. Synthetic procedure for f-FeP, f-NiP and f-NiP/FeP.

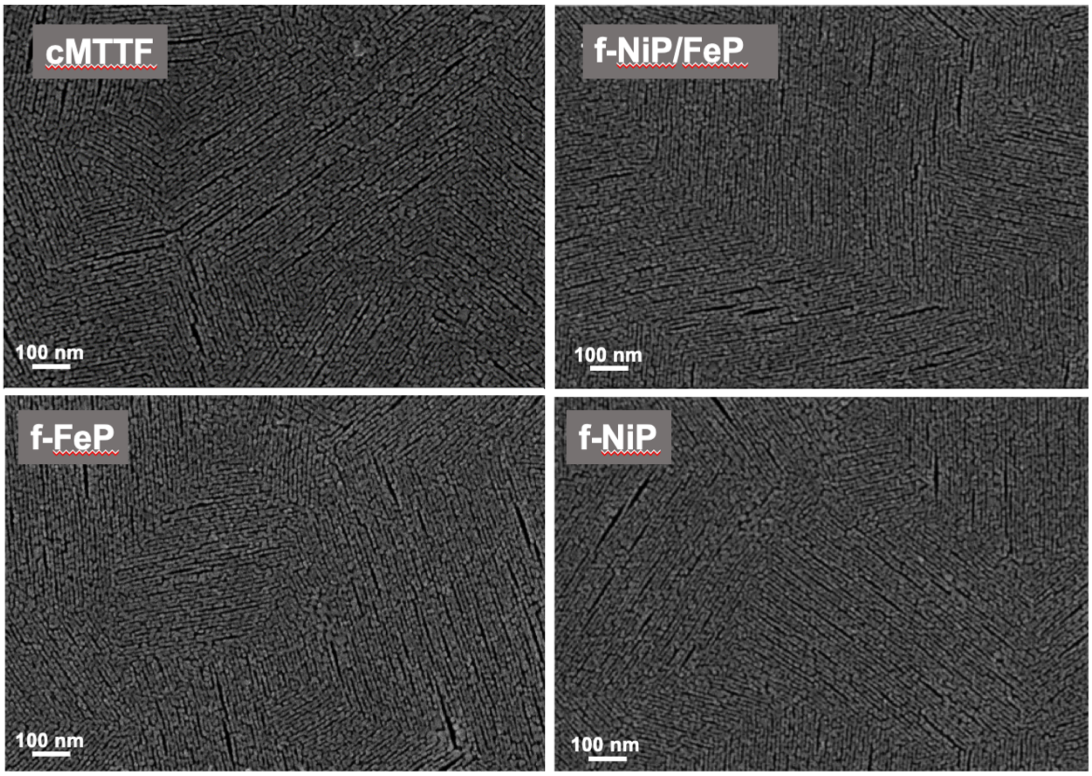

Figure S1. SEM images of cMTTF, f-FeP, f-NiP, and f-NiP/FeP.

Table S1. Assignation of Raman frequencies (cm^{-1}) for the nanocomposites. λ_{exc} = 532 nm.[6]

f-FeP	f-NiP	f-NiP/FeP	Assignation
196	197	198	v Me-N
	245	251	δ porphyrin Ni-O-O según Angnes 2015
	319	321	δ porphyrin trans
394	394	398	γ porphyrin, pyr rot., Fe-P oxidation state marker Ni-O stretching mode, Angnes 2015
	459	462	v Ni2+-O
518	514	522	δ pyridine
561		558	δ porphyrin; v Fe-O2 según Birke 2001
639		641	δ porphyrin
787	792	792	δ porphyrin
		812	v Ni3+-O según Angnes 2015
960	952	956	v pyridine
1010	1012	1011	v porphyrin
1093	1092	1095	δ Cβ – H
1224	1231	1227	δ pyridine
		1280	v Cα-N
1361	1354	1357	v Cα-N; Fe(II)-P oxidation state marker según Birke 2001
	1377	1378	v Cα-N O-O stretching mode, según Angnes 2015
1459		1460	v C_{α}-C_{m} + v C_{α}-C_{β} ó v pyridine
1514	1514	1521	v_{sym} C-C + δ_{asym} porphyrin
1553		1557	v porphyrin; Fe-P oxidation state marker
	1608	1602	v sym C-C
	1639	1639	δ pyridine

v, stretching; γ, folding out of the plane; δ, flection; Me, metal centre

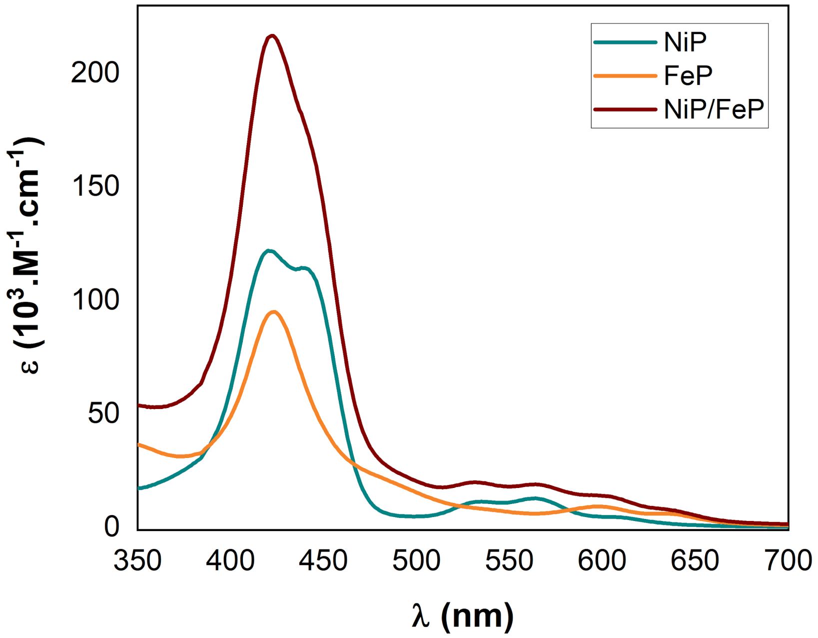

Figure S2. Molar extinction coefficient spectra of FeP, NiP, and NiP/FeP in water.

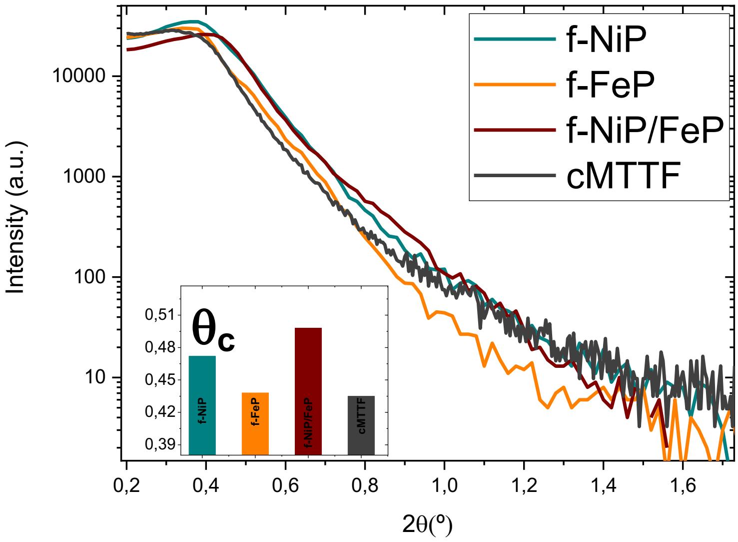

Figure S3. XRR patterns showing the critical angle region for cMTTF, f-NiP, f-FeP, and f-NiP/FeP.

Estimation of NiP, FeP and NiP/FeP loading using XRR data

NiP, FeP and NiP/FeP loading was estimated following the procedure reported previously.[1] The presence of a unique θ_c shifted to higher angle, and the absence of significant changes in the overall thickness of the mesoporous film implies an increase in the density of the thin layer due to the grafting of the porphyrins inside the pore network.

A quantitative analysis can be carried out from XRR data to estimate the pore filling with the porphyrin molecules. It is known that the electronic density ρ_{film} of a mesoporous film can be calculated directly from the measured critical angle, θ_c:

$$\rho_{film} = \frac{\pi}{\lambda^2 r_e}\,\theta_c^2$$

where λ is the X-ray wavelength and r_e=2.813.10^{-6} nm is the classical radius of the electron. From the calculation of the electronic densities for both a mesoporous and a nonporous film, the volume fraction of mesopores, F_{pore}, can be estimated as:

$$F_{pore} = 1 - \frac{\rho_{film}}{\rho_{framework}}$$

where ρ_{film} is the electronic density of the mesoporous film and $\rho_{framework}$ is the electronic density of a non-mesoporous film with the same composition, produced under the same synthesis conditions and treatment, but in the absence of a mesoporous template. Considering that the increase in film density is only due to the presence of porphyrin molecules, the volume fraction of polymer within the film, $F_{Porphyrin}$, can be determined from the measured electronic densities according to:

$$F_{porphyrin} = \frac{\rho_{film+porphyrin} - \rho_{film}}{\rho_{porphyrin}}$$

where $\rho_{film\ porphyrin}$ and ρ_{film} is the electronic density of film after and before the modification, and $\rho_{porphyrin}$ is the porphyrin electronic density calculated taking in mind the chemical formula ($C_{44}H_{36}N_8Ni$; $C_{44}H_{36}N_8Fe$) and the molecular volume (A^3).[2] The mesopore filling fraction was calculated from the ratio between the porphyrin volume fraction $F_{porphyrin}$ and the pore volume fraction F_{pore}.

$$R_{porphyrin} = \frac{F_{porphyrin}}{F_{pore}}$$

The most important implication of these results is that a large fraction of the pore volume is occupied by the porphyrins. These observations are in full agreement with the conclusions derived from UV-vis analysis.

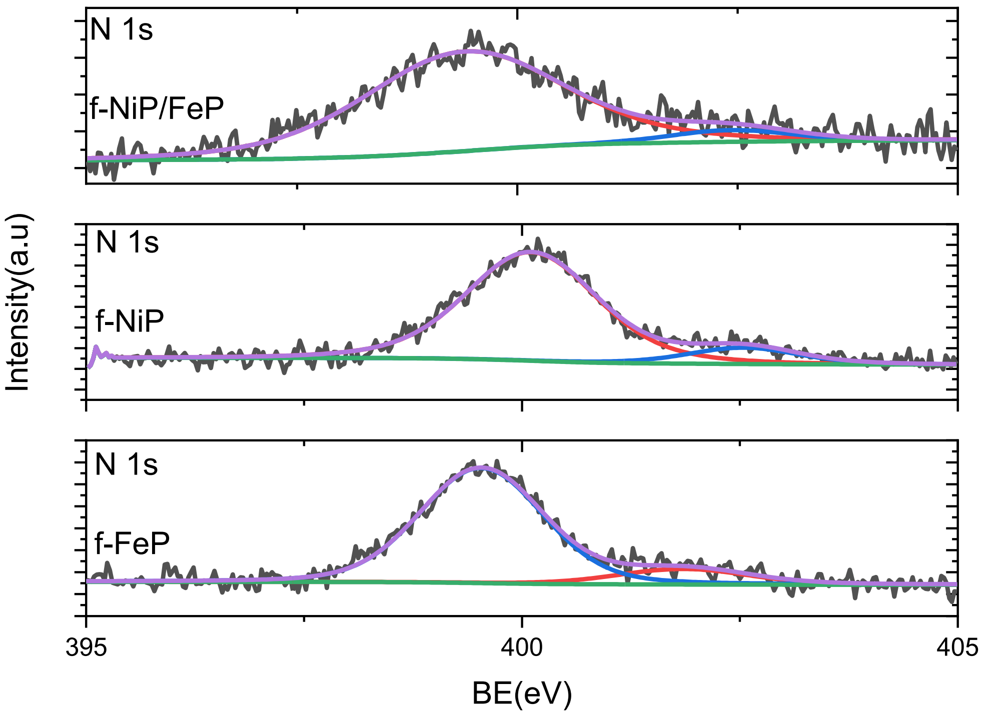

Figure S4. High-resolution XPS spectra of N 1s for f-FeP, f-NiP, and f-NIFeP.

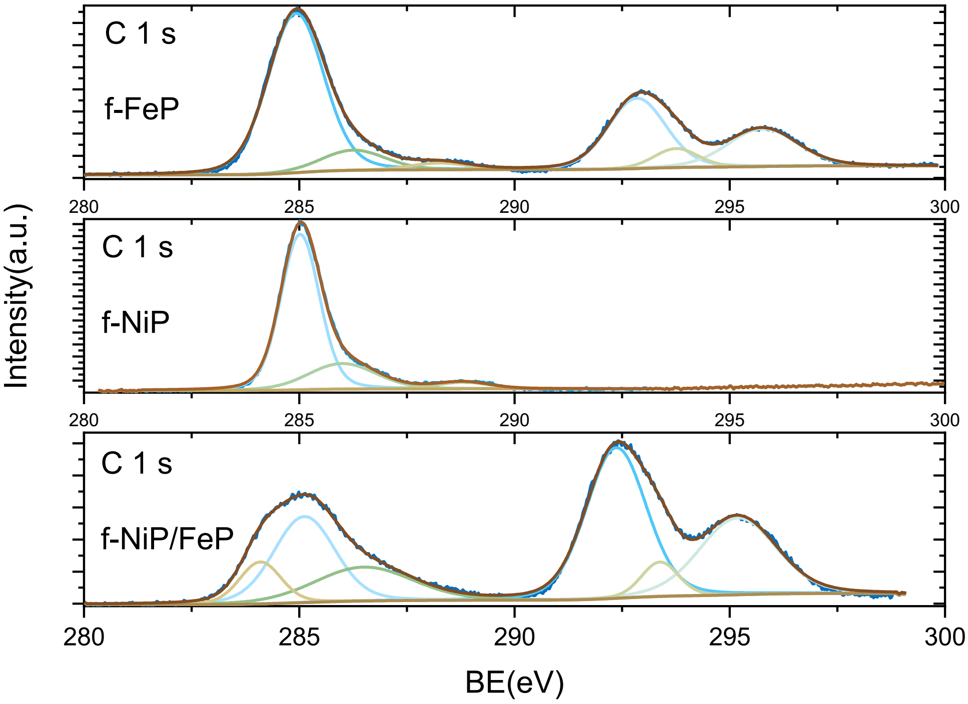

Figure S5. High-resolution XPS spectra of C 1s for f-FeP, f-NiP, and f-NiFeP.

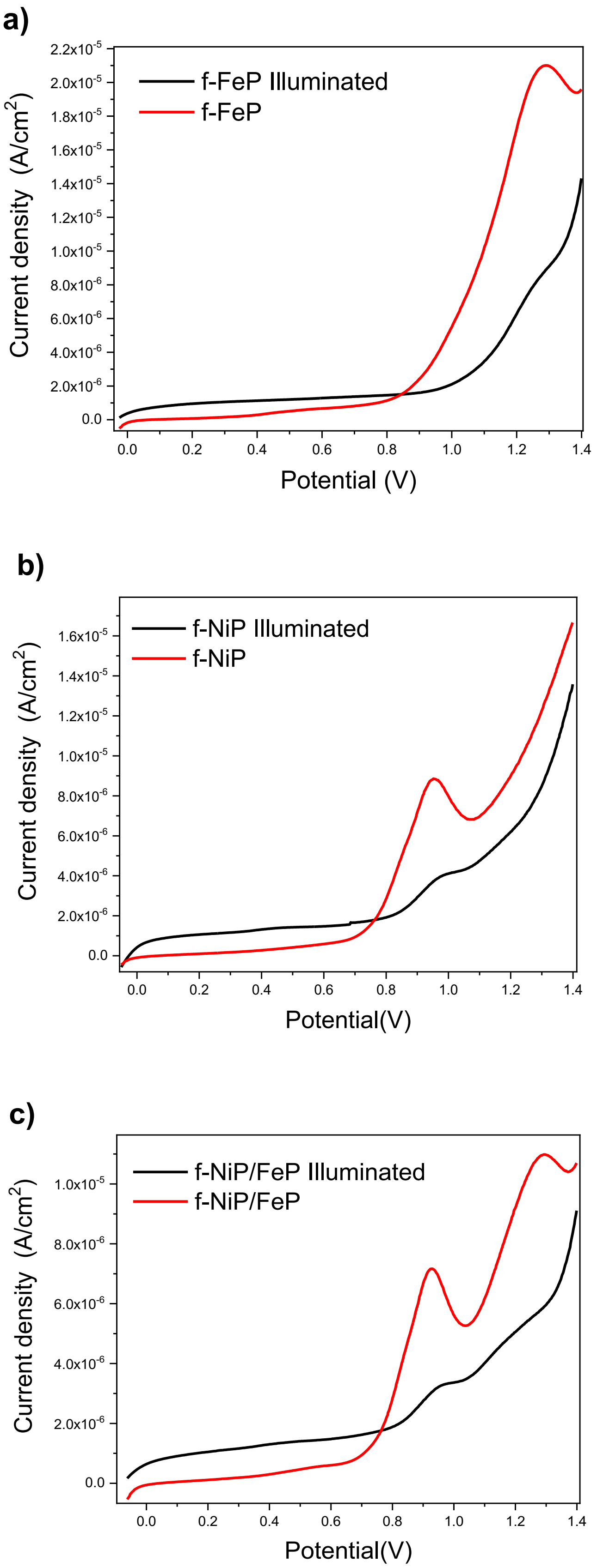

Figure S6. LSV with and without illumination with Xenon lamp, for a) f-FeP, b) f-NiP, and c) f-NiP/FeP (potential vs RHE).

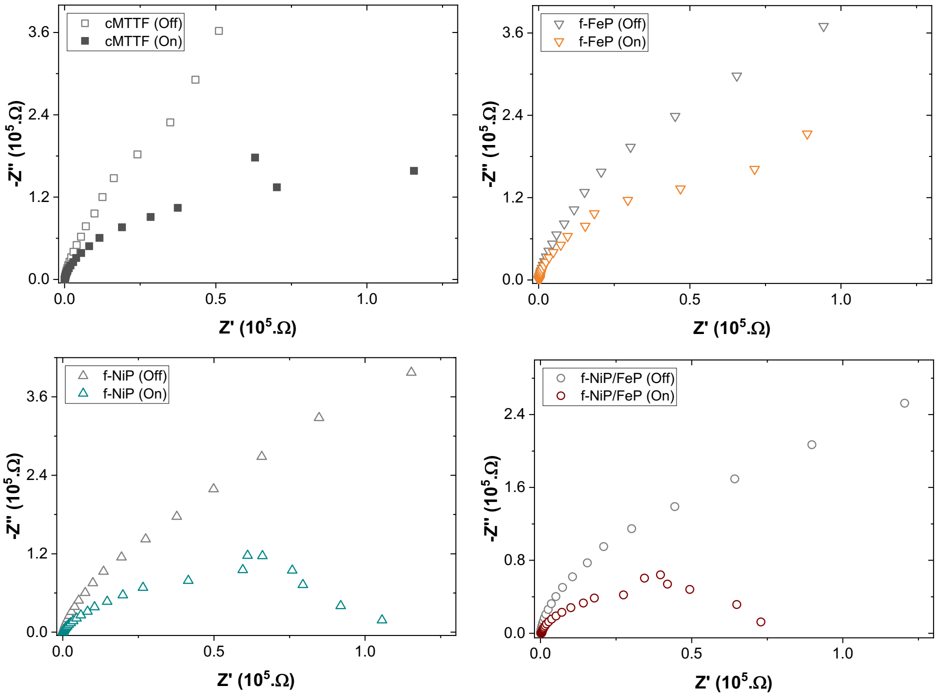

Figure S7. Nyquist diagrams of bare cMTTF, f-FeP, f-NiP, and f-NiP/FeP with (On) and without (Off) light.

Sample	**R[Ω]**	**Rct[Ω]**
cMTTF	74 ± 1	356200 ± 11
f-FeP	237 ± 1	596310 ± 31
f-NiP	83 ± 1	234190 ± 9
f-NiP/FeP	305 ± 11	140120 ± 75

Table S2. Resistance values for the processes were determined by fitting the impedance spectrum of Figure 5.

References

[1] A. Calvo, M.C. Fuertes, B. Yameen, F.J. Williams, O. Azzaroni, G.J.A.A. Soler-Illia, Nanochemistry in Confined Environments: Polyelectrolyte Brush-Assisted Synthesis of Gold Nanoparticles inside Ordered Mesoporous Thin Films, Langmuir. 26 (2010) 5559–5567. doi:10.1021/la9038304.

[2] S.C.M. Gandini, E.L. Gelamo, R. Itri, M. Tabak, Small Angle X-Ray Scattering Study of Meso-Tetrakis (4-Sulfonatophenyl) Porphyrin in Aqueous Solution: A Self-Aggregation Model, Biophys. J. 85 (2003) 1259–1268. doi:10.1016/S0006-3495(03)74561-5.