Electronic Supplementary Information

for

Advances in photo-assisted seawater splitting promoted by green iron oxide-carbon nitride photoelectrocatalysts

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§ S-1. Experimental

§ S-1.1 Synthesis

§ S-1.1.1 $\alpha$-Fe$_2$O$_3$ preparation

Plasma enhanced-chemical vapor deposition (PE-CVD) growth processes were performed using a two-electrode custom-built apparatus equipped with a radio frequency (RF) generator ($v = 13.56$ MHz), adopting Fe(tfa)$_2$TMEDA (tfa = 1,1,1-trifluoro-2,4-pentanedionate; TMEDA = $N,N,N',N'$-tetramethylethylenediamine) as iron precursor.$^1$ Fluorine-doped tin oxide (FTO) glass substrates (Aldrich®; $\approx 7 \, \Omega$/sq; FTO thickness $\approx 600$ nm), subjected to an established pre-cleaning procedure,$^2$ were mounted on the grounded electrode of the PE-CVD reactor, whereas RF-power was applied to the second electrode. Electronic grade Ar and O$_2$ were used as plasma sources. The precursor powders were placed in an external glass reservoir heated at $85^\circ$C by an oil bath, and the vapors were delivered to the deposition zone by an Ar flow [rate = 60 standard cubic centimetres per minute (sccm)] maintaining the feeding lines at $150^\circ$C. Two additional gas-lines were used to introduce Ar (rate = 15 sccm) and O$_2$ (rate = 5 sccm) directly into the reactor. For all depositions, the inter-electrode distance, total pressure, RF-power and process duration were fixed at 6 cm, 1.0 mbar, 20 W and 90 min, respectively. The growth temperature was varied between 100 and $400^\circ$C.

§ S-1.1.2 Carbon nitride preparation

In this work, two different types of graphitic carbon nitride (gCN) powders were prepared using as precursor either melamine [gCN(M)] or a mixture of melamine and cyanuric acid [gCN(CM)]. The former was obtained by melamine (M – Sigma Aldrich) heat treatment in Ar atmosphere at $400^\circ$C for 2 h, to activate melamine condensation to tri-s-triazine, and subsequently at $550^\circ$C for 4 h, to trigger polymerization processes yielding carbon nitride.$^3$ Alternatively, following the synthetic route proposed by Jun et al.$^4$, melamine (M – 1.0 g) and cyanuric acid (CA – Sigma Aldrich; 1.0 g) were dispersed under sonication in 40 mL and 20 mL of dimethylsulfoxide (DMSO), respectively. After heating at $60^\circ$C, the CA-containing mixture was dropped into the M one under continuous stirring, yielding a white suspension of the supramolecular M+CA adduct (CM adduct). After 10 min, the suspension was filtered, and the obtained powder was washed twice with 10 mL ethanol. The recovered solid was heated in Ar at $50^\circ$C for 3 h, and, subsequently, at $500^\circ$C for 2.5 h.
During each electrophoretic deposition (EPD) experiment, the gCN suspension was always maintained under stirring. After a series of preliminary experiments aimed at optimizing the operational conditions and at ensuring the reproducibility of material characteristics, a duration of 20 s was utilized. A potential difference of 10 V was applied using an Agilent E3649A bench power supply. At the end of the process, an ex-situ two-step thermal treatment in air was performed: 1) annealing at 80°C for 1 h (heating rate = 3°C/min); 2) annealing at 520°C for 3 h (heating rate = 20°C/min), followed by a slow cooling to room temperature.

§ S-1.1.3 Functionalization with CoPi

A Co(II) phosphate solution (0.005 M) was prepared by dissolving 16.22 mg of CoCl$_2$•6H$_2$O in 250 mL of a phosphate buffer solution at pH = 7.0. The CoPi deposition procedure on the target photoanodes, optimized basing on the strategy suggested by Nocera et al., was performed as follows:

- 1 CV (cyclic voltammetry) in phosphate buffer (pH = 7.0);
- 1 CV in Co(II) 0.005 M solution in phosphate buffer;
- 1 LSV (linear scan voltammetry) in Co(II) 0.005 M solution in phosphate buffer.

For each scan, a potential range from 0.2 to 1.2 V was adopted.

§ S-1.2 Chemico-physical characterization

X-ray diffraction (XRD) characterization was carried out in glancing incidence mode ($\theta_i = 1.0^\circ$) on a Bruker AXS D8 Advance Plus diffractometer equipped with a Gobel mirror and a CuK$\alpha$ X-ray source ($\lambda = 1.54051$ Å) powered at 40 kV and 40 mA. The analyses were performed at the PanLab facility (Department of Chemical Sciences, Padova University) founded by the MIUR Dipartimento di Eccellenza grant “NExuS”.

Optical absorption spectra were recorded operating in transmittance mode at normal incidence on a Cary 50 (Varian) dual-beam spectrophotometer (spectral bandwidth = 1 nm), using a bare FTO-coated glass substrate as a reference. In all cases, the substrate contribution was subtracted. The band gap ($E_G$) of Fe$_2$O$_3$-containing samples was evaluated using the Tauc relation:

$$ (\alpha h\nu)^n = K(h\nu - E_G) \quad (S1) $$

where $\alpha$, $h\nu$ and $K$ are the absorption coefficient, the photon energy and a constant, respectively,
and $n = 2$ for direct allowed transitions, reported to be the strongest ones for hematite,\textsuperscript{10} the main system component. $E_G$ values were obtained by extrapolating the straight portion of experimental curves to intersect the energy axis at $\alpha = 0$.

For transmission electron microscopy (TEM) analyses, thin cross-sectional samples were prepared using a Thermo Fischer Scientific Helios G4 UC dual beam instrument, located at the PISA facility (GFZ, Potsdam) by the focused ion beam (FIB) technique (Fig. 4 in the main paper). Prior to FIB cutting, a part of the specimen was coated with a liquid silicon glass (Baufan Kali-Wasserglas) to prevent any possible contamination. In the preparation of samples, a Pt layer was deposited to minimize undesired damages/alterations, due to gCN nanostructures fragility under ion beam irradiation. Additional specimens were prepared by scratching, ultrasonication in ethanol and subsequent dispersion on TEM Cu holey carbon grids (see Fig. S12).

As a matter of fact, Fe 2p X-ray photoelectron spectroscopy (XPS) signal deconvolution poses a number of complications. In fact, a reliable fitting must take into account shake-up and plasmon loss structures, as well as multiplet splitting phenomena, all of which can complicate chemical state identification.\textsuperscript{11} As a consequence, in the present study curve fitting of Fe 2p spectra was intentionally avoided. Nevertheless, it is worthwhile highlighting that the XPS results presented and discussed in this work unambiguously indicate the occurrence of Fe$_2$O$_3$ free from other iron oxides in appreciable amounts, in line with the results obtained by the other characterization techniques.

XPS and ultraviolet photoelectron spectroscopy (UPS) valence band spectra were taken after a mild Ar$^+$ erosion (2000 eV, 30 s) using a ThermoFisher Scientific ESCALB\textsuperscript{TM} QXi spectrometer funded by “Sviluppo delle infrastrutture e programma biennale degli interventi del Consiglio Nazionale delle Ricerche (2019). A monochromatic AlK$\alpha$ X-ray source and a He(I) ($h\nu = 21.22$ eV) ultraviolet photon source generated by a helium plasma lamp were employed to collect XPS and UPS valence band spectra, respectively.

Photoluminescence (PL) spectra were recorded using a FLS 1000 fluorimeter (Edinburgh Instruments), adopting the following settings: excitation wavelength/bandwidth = 280/13 nm; emission bandwidth = 7 nm.

\section*{§ S-1.3 Photoelectrochemical tests and related analyses}

The measured potential was converted into the reversible hydrogen electrode (RHE) scale using
the following relation:

\[ E_{\text{RHE}} (V) = E_{\text{WE}} (V) + E_{\text{Ag/AgCl}} (V) + 0.0592 \times \text{pH} \]  \hspace{1cm} (S2)

where \( E_{\text{WE}} \) indicates the bias applied to the working electrode.

The obtained \( E_{\text{RHE}} \) values were subjected to \( iR \) correction according to equation (S3):

\[ E (V) = E_{\text{RHE}} (V) - iR \]  \hspace{1cm} (S3)

where \( i \) is the measured current (in A), and \( R \) the uncompensated cell resistance. The latter was estimated from electrochemical impedance spectroscopy (EIS) as the lowest impedance observed in the high-frequency region of Nyquist plots.\(^{13} \) For all photoelectrocatalysts, the uncompensated resistance ranged between \( \approx 90 \) and \( 100 \ \Omega \). These relatively high resistance values are likely due to the contact between the FTO-supported electrode and the copper foil pressed on its surface, as sketched in Fig. S1. For each electrode, the registered currents were normalized to the geometric sample area (\( \approx 0.28 \ \text{cm}^2 \)).

\[ \text{Fig. S1. Side-view of Zahner photoelectrochemical cell, showing the electrical contact between the copper stripe and the working electrode.} \]

The onset potential was calculated as the one necessary to reach a photocurrent density of 0.02 mA/cm\(^2\).\(^{14} \)

Intensity modulated photocurrent spectroscopy (IMPS) analyses were carried out applying a
LED frequency between 10000 and 0.05 Hz with a 15% of light intensity modulation. The white light intensity was set at 50 mW/cm².

EIS spectra were acquired from 100 mHz to 10 kHz with a potential modulation of 5 mV.

Mott-Schottky plots were obtained at 1 kHz by recording EIS spectra between 0.4 and 1.6 V vs. RHE, with 0.1 V steps. The capacitance value (CSC) was obtained from $Z = R + 1/(i\omega CSC)$, where $Z$ and $R$ are the specimen impedance and resistance, and $\omega$ is the frequency. The flatband potential ($V_{FB}$) was measured by fitting the linear part of $1/CSC^2$ and finding the intercept with the voltage axis, using the equation:

$$\frac{1}{CSC^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_D} \left( V - V_{FB} - \frac{k_BT}{e} \right)$$

where $CSC$ is the capacitance of the semiconductor ($1/C_i^2$, capacitance of the double layer, is considered negligible), $\varepsilon_0$ the permittivity of free space, $\varepsilon_r$ is relative permittivity of the target material, $e$ is the electron charge (C), and $k_B$ is the Boltzmann constant. The majority carrier concentration ($N_D$) was obtained from the slope of the linear part of $1/CSC^2$. The value for the Fermi level energy ($E_F$) was assumed to be coincident with $V_{FB}$ and was used to construct the diagram of Fig. 6.

Iodometric titration was used for the identification of possible hypochlorite species generated during the process, following a previously described procedure. In this case, ClO⁻, if present, oxidizes I⁻ species in alkaline solution according to the reaction:

$$H_2O + ClO^-(aq) + 2I^-(aq) \rightarrow I_2 + Cl^-(aq) + 2OH^-(aq)$$

The obtained I₂ subsequently forms polyiodide ions, like I₃⁻, that in the presence of starch yield an intensely blue colored complex. The appearance of the latter can be considered as a fingerprint of hypochlorite presence.
§ S-2. Characterization

§ S-2.1 Optimization of iron(III) oxide growth conditions

In this work, preliminary attention was devoted to the optimization of iron(III) oxide growth by PE-CVD, with particular regard to the evolution of material structural, morphological and optical properties as a function of the adopted preparative conditions. The system structure was investigated by XRD. As can be observed in Fig. S2, whereas at 100°C no diffraction peaks were evident, for temperatures \( \geq 200°C \) the recorded patterns were characterized by reflections pertaining to rhombohedral \( \alpha-\text{Fe}_2\text{O}_3 \) (hematite) as the sole iron(III) oxide polymorph.\(^{18} \) A comparison with the reference pattern suggested a preferential (110) growth for \( T \geq 300°C \), that may account for an improved electron transport, resulting in enhanced photoelectrochemical performances.\(^{10} \)

![XRD patterns](image)

**Fig. S2.** XRD patterns of \( \text{Fe}_2\text{O}_3 \) deposits on FTO obtained at different growth temperatures. The pattern pertaining to the FTO-coated glass substrate is also reported for comparison. All the indexed peaks correspond to \( \alpha-\text{Fe}_2\text{O}_3 \) (hematite) reflections.\(^{18} \)

Optical absorption spectra (Fig. S3), consistent with those previously reported for pure iron(III) oxide nanomaterials,\(^{10} \) showed a progressive absorbance increase with deposition temperature throughout the whole wavelength range. The calculated optical band gaps (\( E_G = 2.08 \pm 0.06 \) eV) were in good agreement with those for \( \text{Fe}_2\text{O}_3 \).\(^{2} \)
The system morphological features were investigated by field emission-scanning electron microscopy (FE-SEM, Fig. S4). The specimen obtained at 100°C featured a compact globular organization, whereas at 200°C the deposit presented interconnected wheat-ear shaped structures perpendicular to the FTO substrate surface. In a different way, specimens prepared at 300°C and 400°C presented lamellar aggregates, whose assembly resulted in high active area materials. The latter can favor gCN dispersion even in the inner sample regions, promoting a close Fe$_2$O$_3$/gCN contact. In addition, their hierarchical porous structure offers a short diffusion channel for ion and mass transportation, highly beneficial for seawater penetration.\textsuperscript{13}

Basing on the above data, the sample grown at 400°C was selected as the most promising one.
for the subsequent functionalization with gCN and CoPi thanks to its higher crystallinity, improved optical absorption, and favorable morphological features.

Fig. S4. Representative plane-view (left) and cross-sectional (right) FE-SEM images of Fe₂O₃ deposits grown on FTO at different temperatures.
§ 2.2 Chemico-physical characterization of electrode materials

![EDXS spectrum for a Fe$_2$O$_3$-CM specimen.]

**Fig. S5.** Top: representative energy-dispersive X-ray spectroscopy (EDXS) spectrum for a Fe$_2$O$_3$-CM specimen. Bottom: plane view FE-SEM images, corresponding EDXS maps on the selected areas, and related quantitative analyses for Fe$_2$O$_3$-M and Fe$_2$O$_3$-CM. C and O contents are also affected by adventitious contamination (see XPS results) and the underlying FTO substrate, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C Kα</th>
<th>N Kα</th>
<th>O Kα</th>
<th>Fe Kα</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$-M</td>
<td>3.0</td>
<td>4.0</td>
<td>50.0</td>
<td>43.0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-CM</td>
<td>4.0</td>
<td>3.8</td>
<td>49.5</td>
<td>42.7</td>
</tr>
</tbody>
</table>
Fig. S6. (a) XRD patterns, (b) optical absorption spectra, and (c) Tauc plots of Fe$_2$O$_3$, Fe$_2$O$_3$-M and Fe$_2$O$_3$-CM specimens.
Fig. S7. Representative FE-SEM images for specimens \( \text{Fe}_2\text{O}_3\)-M-CoPi (a,b) and \( \text{Fe}_2\text{O}_3\)-CM-CoPi (c,d). (e) EDXS spectrum for sample \( \text{Fe}_2\text{O}_3\)-CM-CoPi. Phosphorus presence confirms the successful system functionalization with CoPi.

FE-SEM images in Fig. S7a-d demonstrate that CoPi deposition leads to aggregates homogeneously distributed over the underlying deposits and featuring various shapes and dimensions. CoPi presence is also demonstrated by EDXS analyses (Fig. S7e).
Fig. S8. XPS wide scan spectra for bare Fe₂O₃ and gCN-functionalized specimens.

XPS wide scan spectra (Fig. S8) clearly show iron and oxygen signals even for carbon nitride-functionalized systems, in line with the surface presence of very small gCN amounts [as confirmed by transmission electron microscopy (TEM) analyses]. The absence of tin signals proved the complete coverage of the FTO substrate.

For both bare iron oxide and the composite materials, the O/Fe atomic percentage (at. %) ratio values (2.2-2.3) were higher than the one expected for stoichiometric Fe₂O₃ (O/Fe = 1.5), due to the chemisorption of -OH groups on surface defects.²,⁶,⁷ The obtained O/Fe values slightly higher after CoPi introduction, as expected.
Fig. S9. Surface C1s photoelectron peaks for specimens Fe$_2$O$_3$-M (a) and Fe$_2$O$_3$-CM-CoPi (b). Color codes as in Fig. 2.

Table S1. BE (eV) and % of the various C1s components with respect to the overall C1s peak for the indicated specimens. Color codes as in Fig. 2.
Fig. S10. (a) N1s, (b) Co2p, and (c) P2p photoelectron peaks for sample Fe₂O₃-CM-CoPi. Co at.% was estimated to be \( \approx 3.0 \). Color codes for (a) as in Fig. 2.

Table S2. BE (eV) and % of the various N1s components with respect to the overall N1s peak for the indicated specimens. Color codes as in Fig. 2. The component associated to \( \pi \)-electron excitations in the heptazine rings of carbon nitride, expected at BE \( \approx 404.2 \) eV and much weaker than the other ones,\(^ {3,19-21} \) could not be detected due to the low overall nitrogen content.
Table S3. BE (eV) of Fe2p spin-orbit components for the target specimens. SOS = spin-orbit splitting.

<table>
<thead>
<tr>
<th>sample</th>
<th>BE (Fe2p3/2) (eV)</th>
<th>BE (Fe2p1/2) (eV)</th>
<th>SOS (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>711.2</td>
<td>724.7</td>
<td>13.5</td>
</tr>
<tr>
<td>Fe₂O₃-M</td>
<td>711.0</td>
<td>724.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Fe₂O₃-CM</td>
<td>710.9</td>
<td>724.4</td>
<td>13.5</td>
</tr>
<tr>
<td>Fe₂O₃-CM-CoPi</td>
<td>710.9</td>
<td>724.4</td>
<td>13.5</td>
</tr>
</tbody>
</table>

For specimen Fe₂O₃-CM-CoPi (Fig. S10), both the Co2p and the P2p signals were clearly discernible. As regards the Co2p photpeak, the signal energy location [BE(2p₂/3) = 780.8; SOS = 15.4 eV] was in line with literature results for similar functionalized systems.¹⁰,²² In particular, basing on the shape of shake-up satellites at BE ≈ 7.6 eV higher than the corresponding spin-orbit split components, as well as the BE separation among the 2p₃/2 and 2p₁/2 components of ≈ 15.4 eV, cobalt centers were deemed to be primarily present as Co(II), with a likely minor contribution from Co(III) species.²³

The P2p photpeak revealed the occurrence of phosphate groups in a single chemical environment [BE(P2p₃/2) = 132.4; SOS = 0.84 eV],²³⁻²⁶ excluding the formation of phosphide moieties.²⁷,²⁸ Overall, these results proved the successful deposition of CoPi on the target samples.
**Fig. S11.** Surface O1s photoelectron peaks for the indicated samples. Color codes as in Table S4.

For all CoPi-free samples, two different components contributed to the O1s signal (Fig. S11): the main one, O_0, related to lattice oxygen in Fe_2O_3,^{29-35} and a second band, O_1, assigned to -OH groups adsorbed on surface vacancies.^{8, 9, 25, 36-41} After functionalization with CoPi, a third component, ascribed to the presence of cobalt phosphate, could be identified (O_{CoPi}; see Table S4).^{23, 25}

Upon going from bare Fe_2O_3 to Fe_2O_3-M and Fe_2O_3-CM, the O_0 component underwent a progressive red shift (see also Table S4), whose entity was the same as the one experienced by Fe2p signals (compare Table S3). This variation confirmed the formation of a type-II Fe_2O_3/gCN heterojunction, as discussed in the main paper text, with a more efficient charge transfer occurring for Fe_2O_3-CM in comparison to Fe_2O_3-M.
<table>
<thead>
<tr>
<th>Sample</th>
<th>O&lt;sub&gt;0&lt;/sub&gt;</th>
<th>O&lt;sub&gt;CoPi&lt;/sub&gt;</th>
<th>O&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE (eV)</td>
<td>%</td>
<td>BE (eV)</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>529.9</td>
<td>80.3</td>
<td>-</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-M</td>
<td>529.7</td>
<td>85.8</td>
<td>-</td>
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<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CM</td>
<td>529.6</td>
<td>81.9</td>
<td>-</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CM-CoPi</td>
<td>529.6</td>
<td>69.6</td>
<td>530.8</td>
</tr>
</tbody>
</table>

**Table S4.** BE (eV) and % of the various O1s components with respect to the overall O1s peak for the target specimens.
**Fig. S12.** HAADF-STEM overview and corresponding EDXS-STEM elemental maps of Fe K, O K, N K and overlaid color image for specimens Fe$_2$O$_3$-CM (a) and Fe$_2$O$_3$-M (b). Nitrogen signals, although very weak, well reproduced the surface morphology of the underlying iron oxide, suggesting the presence of a uniform and very thin gCN layer.
**Fig. S13.** XPS (a,c) and UPS (b,d) valence band spectra for gCN(CM) and Fe$_2$O$_3$ ($E_F$ = Fermi level energy; VB = valence band).
Fig. S14. Photoluminescence spectra obtained from Fe$_2$O$_3$, Fe$_2$O$_3$-CM and Fe$_2$O$_3$-CM-CoPi specimens.

The three PL spectra obtained for Fe$_2$O$_3$, Fe$_2$O$_3$-CM and Fe$_2$O$_3$-CM-CoPi samples (Fig. S14) show a very weak luminescence with negligible differences. As reported in the literature, Fe$_2$O$_3$ in bulk form, and with sufficiently developed crystalline particles, does not present any PL due to the local d-band transition nature and efficient energy relaxation.$^{42, 43}$ We also attribute the lack of photoluminescence at 450 nm, typical of gCN, to the very low carbon nitride amount present in the target nanocomposites, and to the PL quenching due to the Fe$_2$O$_3$/gCN junction formation.
§ S-2.3. Photoelectrochemical tests and related analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>$j_{1.5}$ (mA/cm²)</th>
<th>Onset potential @ 0.02 mA/cm² (V vs. RHE)</th>
<th>Tafel slope (mV/dec)</th>
<th>$\text{ABPE}_{\text{max}} \times 10^3$ (%)</th>
<th>$E_{\text{Wmax}}$ (V_{RHE})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td></td>
<td>0.50</td>
<td>1.16</td>
<td>141</td>
<td>3.68</td>
<td>1.08</td>
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<tr>
<td>Fe$_2$O$_3$-M</td>
<td></td>
<td>0.61</td>
<td>1.15</td>
<td>133</td>
<td>4.65</td>
<td>1.07</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-CM</td>
<td>Simulated alkaline seawater (0.5 M KOH + 0.5 M NaCl)</td>
<td>0.65</td>
<td>1.11</td>
<td>124</td>
<td>7.61</td>
<td>1.03</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-CoPi</td>
<td></td>
<td>0.68</td>
<td>1.07</td>
<td>111</td>
<td>12.84</td>
<td>1.03</td>
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<tr>
<td>Fe$_2$O$_3$-M-CoPi</td>
<td></td>
<td>0.76</td>
<td>1.06</td>
<td>108</td>
<td>13.44</td>
<td>1.02</td>
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<td>Fe$_2$O$_3$-CM-CoPi</td>
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<td>0.85</td>
<td>1.03</td>
<td>102</td>
<td>26.40</td>
<td>0.98</td>
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Table S55. Oxygen evolution reaction (OER) performances for photoelectrocatalysts based on Fe$_2$O$_3$ and gCN, both as such and functionalized with CoPi, in simulated alkaline seawater splitting. $j_{1.5}$ corresponds to the current density measured at 1.5 V vs. RHE. The potential of maximum efficiency ($E_{\text{Wmax}}$) corresponds to the maximum in each of the applied bias photon-to-current efficiency (ABPE) curves in Fig. 5b.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>$j_{1.5}$ (mA/cm²)</th>
<th>Onset potential @ 0.02 mA/cm² (V vs. RHE)</th>
<th>Tafel slope (mV/dec)</th>
<th>$\text{ABP}_{\text{max}} \times 10^3$ (%)</th>
<th>$E_{\text{Wmax}}$ (V_{RHE})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$-CoPi</td>
<td></td>
<td>0.66</td>
<td>1.15</td>
<td>144</td>
<td>5.13</td>
<td>1.07</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-M-CoPi</td>
<td>Real alkaline seawater (pH: 13.58)</td>
<td>0.71</td>
<td>1.10</td>
<td>136</td>
<td>6.40</td>
<td>1.06</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-CM-CoPi</td>
<td></td>
<td>0.79</td>
<td>1.09</td>
<td>125</td>
<td>7.94</td>
<td>1.05</td>
</tr>
</tbody>
</table>

**Table S6.** OER performances for photoelectrocatalysts based on Fe$_2$O$_3$ and gCN functionalized with CoPi, in Adriatic seawater splitting. $E_{\text{Wmax}}$ values correspond to the maxima in ABPE curves displayed in Fig. 7b.
<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte</th>
<th>$j_{1.5}$ (mA/cm$^2$)</th>
<th>Tafel slope (mV/dec)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-doped g-C$_3$N$_4$ (^a)</td>
<td>Simulated alkaline seawater (1.0 M KOH + 0.5 M NaCl)</td>
<td>≈1</td>
<td>354.9</td>
<td>12</td>
</tr>
<tr>
<td>NiFe (LDH)/Mo-doped g-C$_3$N$_4$ (^a)</td>
<td></td>
<td>≈1-5</td>
<td>≈133-169</td>
<td>12</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (^b)</td>
<td>Simulated alkaline seawater (1.0 M NaOH + 35 g/L sea salt)</td>
<td>≈0.35</td>
<td>n.a.</td>
<td>14</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-TiO$_2$ (^b)</td>
<td></td>
<td>≈1.0</td>
<td>n.a.</td>
<td>14</td>
</tr>
</tbody>
</table>

Table S7. OER performances for previously reported electrocatalysts based on Fe$_2$O$_3$ or gCN in simulated seawater splitting. \(^a\) dark conditions. \(^b\) light conditions. LDH = layered double hydroxides. n.a. = not available.
<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte</th>
<th>$j_{1.5}$ (mA/cm$^2$)</th>
<th>Tafel slope (mV/dec)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$@g-C$_3$N$_4$ $^a$</td>
<td>Natural seawater (pH = 6.4)</td>
<td>$\approx 1.3$</td>
<td>n.a.</td>
<td>44</td>
</tr>
<tr>
<td>TiO$_2$@g-C$_3$N$_4$@CoPi $^a$</td>
<td></td>
<td>$\approx 1.7$</td>
<td>n.a.</td>
<td>44</td>
</tr>
<tr>
<td>WO$_3$@g-C$_3$N$_4$ $^a$</td>
<td></td>
<td>$\approx 0.95$</td>
<td>n.a.</td>
<td>45</td>
</tr>
<tr>
<td>Ru, Ni-doped Fe$_2$O$_3$ $^b$</td>
<td>Real alkaline seawater (1.0 M KOH)</td>
<td>$\approx 0$</td>
<td>$\approx 60-80$</td>
<td>35</td>
</tr>
</tbody>
</table>

Table S8. OER performances for previously reported electrocatalysts based on Fe$_2$O$_3$ or gCN in seawater splitting. $^a$ light conditions. $^b$ dark conditions. n.a. = not available.
**Fig. S15.** Mott-Schottky plots as a function of the applied potential for specimens Fe$_2$O$_3$-M, Fe$_2$O$_3$-CoPi, and Fe$_2$O$_3$-M-CoPi.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{FB}$ vs. RHE (V)</th>
<th>$N_D$ (m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.86</td>
<td>2.1×10$^{26}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-M</td>
<td>0.82</td>
<td>5.4×10$^{26}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-CM</td>
<td>0.80</td>
<td>7.2×10$^{26}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-CoPi</td>
<td>0.80</td>
<td>9.8×10$^{26}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-M-CoPi</td>
<td>0.78</td>
<td>1.0×10$^{27}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-CM-CoPi</td>
<td>0.74</td>
<td>1.1×10$^{27}$</td>
</tr>
</tbody>
</table>

**Table S9.** Flat band potentials ($V_{FB}$) and majority charge carrier concentration ($N_D$) obtained from Mott-Schottky plots at 1 kHz.
Fig. S16. Incident photon-to-current conversion efficiency (IPCE, %) spectra for Fe$_2$O$_3$ (a), Fe$_2$O$_3$-M (b), Fe$_2$O$_3$-CM (c), and Fe$_2$O$_3$-M-CoPi (d).
Intensity modulated photocurrent spectroscopy (IMPS) is a form of impedance spectroscopy measuring the photocurrent phase shift in relation to a sinusoidal modulation of the light source\textsuperscript{46,47}. The IMPS response as a function of frequency can be expressed as:

\[ j_{\text{photo}} = j_{\text{hole}} \frac{C_H}{C_H + C_{SC}} \frac{(k_{\text{inj}} + i\omega)}{(k_{\text{inj}} + i\omega + k_{\text{rec}} + i\omega)} \left[ \frac{1}{1 + i\omega \tau_c} \right] \]

(S6)

where \( \tau_c \) is the cell time constant, \( k_{\text{rec}} \) and \( k_{\text{inj}} \) are pseudo-first order rate constants for electron-hole recombination and charge injection (in the electrolyte), respectively, and \( j_{\text{hole}} \) is the photocurrent density before recombination. \( C_H \) and \( C_{SC} \) are the capacitances of the Helmholtz layer and the space charge region, respectively. A normalized and simulated Nyquist plot \( \frac{j_{\text{photo}}}{j_{\text{hole}}} \) is reported in Fig. S17. Assuming that \( \tau_c \) is at least two decades smaller than \( 1/(k_{\text{rec}} + k_{\text{inj}}) \), two important numbers can be identified in the plot, i.e. the low frequency intercept (LFI):

\[ \text{LFI} = j_{\text{hole}} \frac{C_H}{C_H + C_{SC}} \frac{(k_{\text{inj}})}{(k_{\text{inj}} + k_{\text{rec}})} \]

(S7)

and the high frequency intercept (HFI):

\[ \text{HFI} = j_{\text{hole}} \frac{C_H}{C_H + C_{SC}} \]

(S8)

as indicated in Fig. S17. Combining equations (S7) and (S8), the ratio HFI/LFI corresponds to \( \frac{k_{\text{inj}}}{(k_{\text{inj}} + k_{\text{rec}})} \).

The other interesting point in Fig. S17 corresponds to the resonance frequency (the maximum in the positive quadrant): \( \omega_{\text{max}} = k_{\text{inj}} + k_{\text{rec}} \). Since \( \omega_{\text{max}} \) can be easily obtained from the Nyquist plot, it is straightforward to calculate \( k_{\text{inj}} \) and \( k_{\text{rec}} \).

In Figs. S18 and S19, each spectrum is normalized to ensure that the HFI = \( \frac{C_H}{C_H + C_{SC}} \).
Fig. S17. Simulated IMPS Nyquist plot. The points in the figure enabling to calculate $k_{\text{inj}}$ and $k_{\text{rec}}$ are LFI, HFI and $\omega_{\text{max}}$, indicated by arrows. The high frequency intercept should occur at unity, since the measured current is equal to the hole current (i.e. no recombination), assuming $C_H/(C_H+C_{\text{SC}}) \approx 1$. The normalized low frequency intercept corresponds to the fraction of the hole flux that undergoes interfacial electron transfer, $k_{\text{inj}}/(k_{\text{inj}}+k_{\text{rec}})$. 
Fig. S18. (a) $k_{inj}$, (c) $k_{rec}$, and (e) charge transfer efficiency values ($\eta_{eff}$, defined as in the main paper text, Fig. 8 caption) for samples Fe$_2$O$_3$-CoPi, Fe$_2$O$_3$-M-CoPi and Fe$_2$O$_3$-CM-CoPi. IMPS measurements were carried out in 0.1 M KOH aqueous solutions, before electrochemical tests in seawater. The corresponding normalized Nyquist IMPS plots are displayed in (b), (d) and (f).
Fig. S19. Normalized Nyquist IMPS plots for samples Fe$_2$O$_3$-CoPi (a), and Fe$_2$O$_3$-M-CoPi (b). IMPS measurements were carried out in 0.1 M KOH aqueous solutions, after testing the specimens in seawater.
§ S-2.4 Characterization after photoelectrochemical tests

Fig. S20. XPS analysis for the indicated specimens after storage under ambient conditions for six months, during which each sample was photoelectrochemically tested in Adriatic seawater every 90 days: (a) C1s, (b) N1s, (c) O1s, and (d) Fe2p photoelectron peaks.
Fig. S21. XPS analysis for Fe$_2$O$_3$-CM-CoPi after storage under ambient conditions for six months, during which the sample was photoelectrochemically tested in Adriatic seawater every 90 days: (a) P2p, and (b) Co2p photoelectron peaks. Compared to the Co2p signals detected on the same sample prior electrochemical tests (see Fig. S10b), the BE separation between the main spin orbit components slightly decreased to 15.2 eV, suggesting a likely increase of the Co(III)/Co(II) ratio, in line with literature results on similar CoPi-containing systems.$^{23}$
**Fig. S22.** Atomic percentage (%) values for the indicated specimens before photoelectrochemical tests (in blue), and after storage under ambient conditions for six months (in orange), during which each sample was photoelectrochemically tested in Adriatic seawater every 90 days.
Fig. S23. XRD patterns of Fe$_2$O$_3$-M-CoPi and Fe$_2$O$_3$-CM-CoPi specimens after storage under ambient conditions for six months, during which each sample was photoelectrochemically tested in Adriatic seawater every 90 days. The pattern of the FTO-coated glass substrate is also reported for comparison. All the indexed peaks correspond to α-Fe$_2$O$_3$ (hematite) reflections.$^{18}$ CoPi presence could never be revealed, due to its low amount (compare Fig. S10 caption) and/or amorphous nature.$^{48,49}$
Fig. S24. Representative FE-SEM micrographs for specimens Fe$_2$O$_3$-M-CoPi (a) and Fe$_2$O$_3$-CM-CoPi (b) after storage under ambient conditions for six months, during which each sample was photoelectrochemically tested in Adriatic seawater every 90 days.
References


