

Supporting Information

*for*

**Functionalization of graphitic carbon nitride systems by cobalt and cobalt-iron oxides boosts solar water oxidation performances**

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## ***§ S1. Additional experimental details***

### *§ S1-1. Synthesis*

Carbon nitride powders used as precursors for the target materials were synthesized by thermal condensation of melamine. In particular, 2 g of melamine (99%, Sigma-Aldrich) were placed in an oven under inert atmosphere (Ar) and heated in three steps with constant rate (2°C/min) at 100°C (30 min), 400°C (2:30 h), and finally 550°C (4 h). A yellowish compact powder was obtained (see Fig. 1 of the main paper text, upper green panel).

### *§ S1-2. Chemico-physical characterization and photoelectrochemical tests*

X-ray photoelectron spectroscopy (XPS) survey scans were acquired in the 0–1100 eV energy range (187.85 eV pass energy, 0.800 eV×step<sup>-1</sup>, 20 msec×step<sup>-1</sup>). Higher resolution photopeaks were registered using the following experimental settings: 58.70 eV pass energy, 0.125 eV×step<sup>-1</sup>, 50 msec×step<sup>-1</sup>.

Energy-dispersive X-ray spectroscopy (EDXS) analyses were performed using an INCA x-act PentaFET Precision spectrometer connected to a Zeiss SUPRA 40VP instrument, at a primary beam voltage of 20 kV.

X-ray diffraction (XRD) measurements were carried out by a Bruker AXS D8 Advance Plus diffractometer equipped with a Göbel mirror and a CuK $\alpha$  X-ray source ( $\lambda = 1.54051 \text{ \AA}$ ) powered at 40 kV, 40 mA. The analyses were carried out at the PanLab facility (Department of Chemical Sciences, Padova University) founded by the MIUR Dipartimento di Eccellenza grant “NExuS”.

FT-IR spectra were registered on a JASCO 4100 instrument in attenuated total reflectance (ATR) mode (PIKE IRIS ATR).

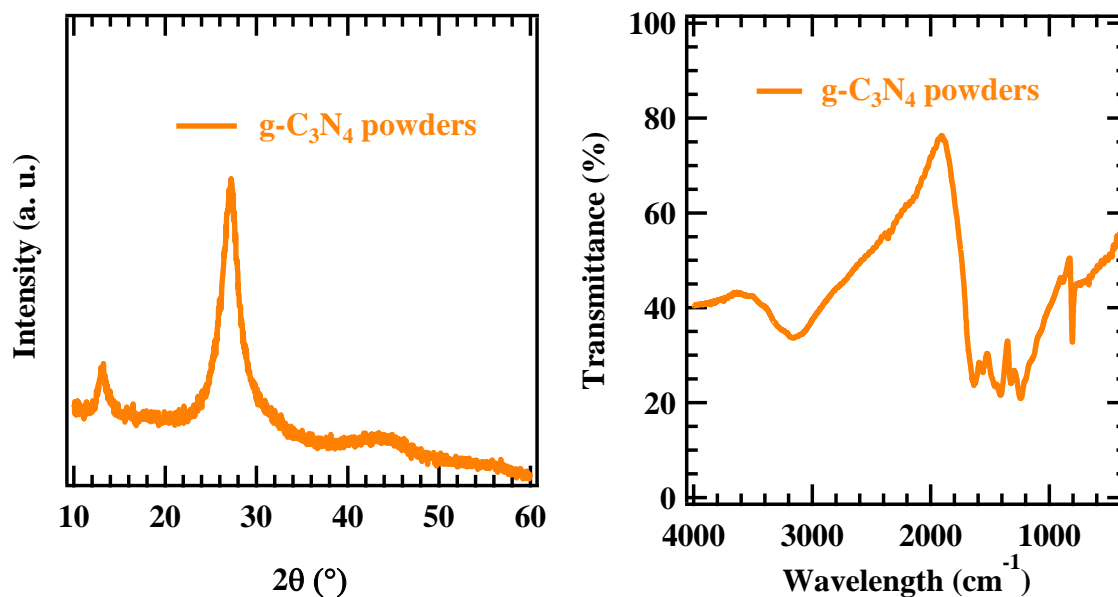
Samples for transmission electron microscopy (TEM) observations were prepared by mechanically scratching the surface of the glass substrate in a dry state and subsequent deposition on a TEM Quantifoil grid. TEM image processing was performed using an open source HyperSpy [1] Python

software package. Simulated electron diffraction data as well as high-resolution STEM images were calculated using JEMS [2] software. Dual electron energy loss spectroscopy (EELS) was used to get absolute energy of the Co *L*, O *K* and Fe *L* edges.

After each photoelectrochemical test, the KOH 0.1 M electrolyte solution was regularly changed, and the standard calomel electrode (SCE) potential recalibrated in order to ensure a full reproducibility of the results obtained in repeated experiments.

Tafel slopes were calculated using polarization curves by plotting potential [vs. the standard hydrogen electrode (RHE)] against log(current density).

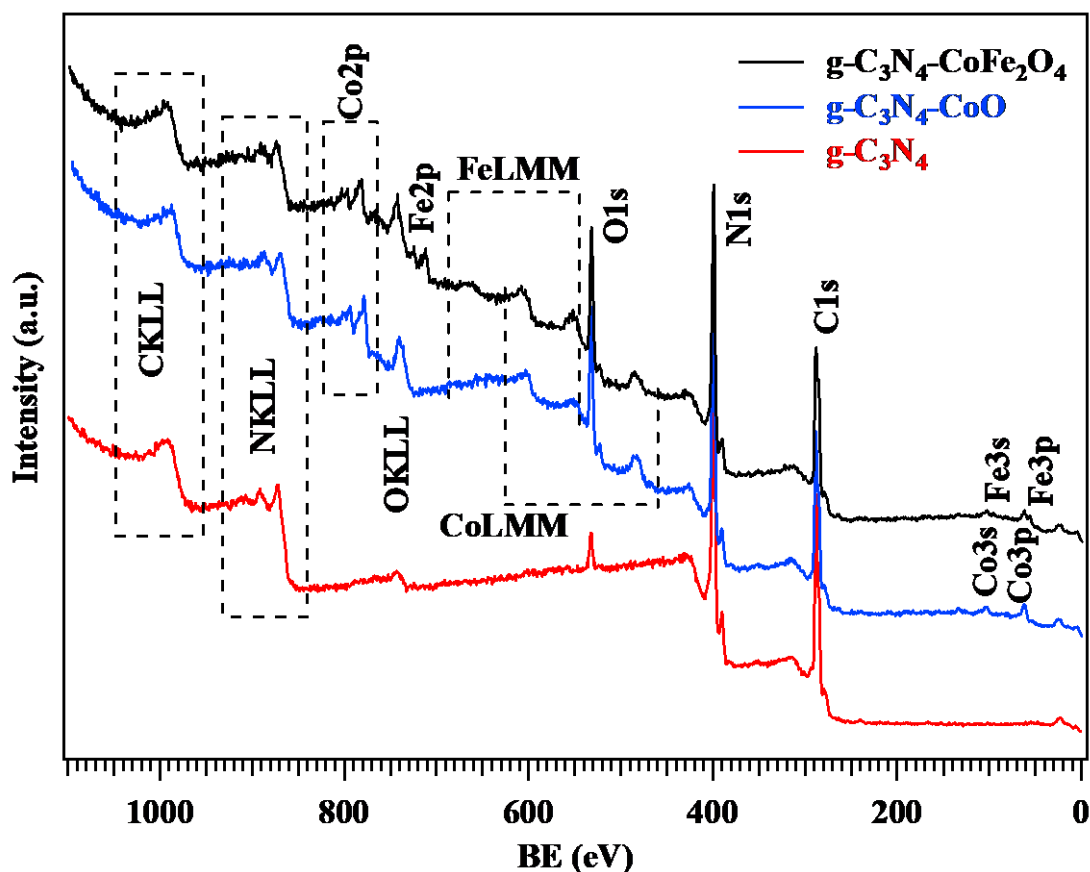
## § S2. Material chemico-physical characterization



**Fig. S1.** XRD pattern recorded in the Bragg-Brentano geometry (left) and FT-IR spectrum (right) for carbon nitride powders used as precursors for the preparation of fluorine-doped tin oxide (FTO)-supported materials.

In the XRD pattern of Fig. S1, left panel, the signal at  $2\theta = 13.1^\circ$  was associated to the in-plane packing of tri-s-triazine units in the (100) crystallographic plane [3-4], whereas the diffraction peak at  $2\theta = 27.2^\circ$  was related to the (002) plane corresponding to the interplanar stacking of carbon nitride sheets [5].

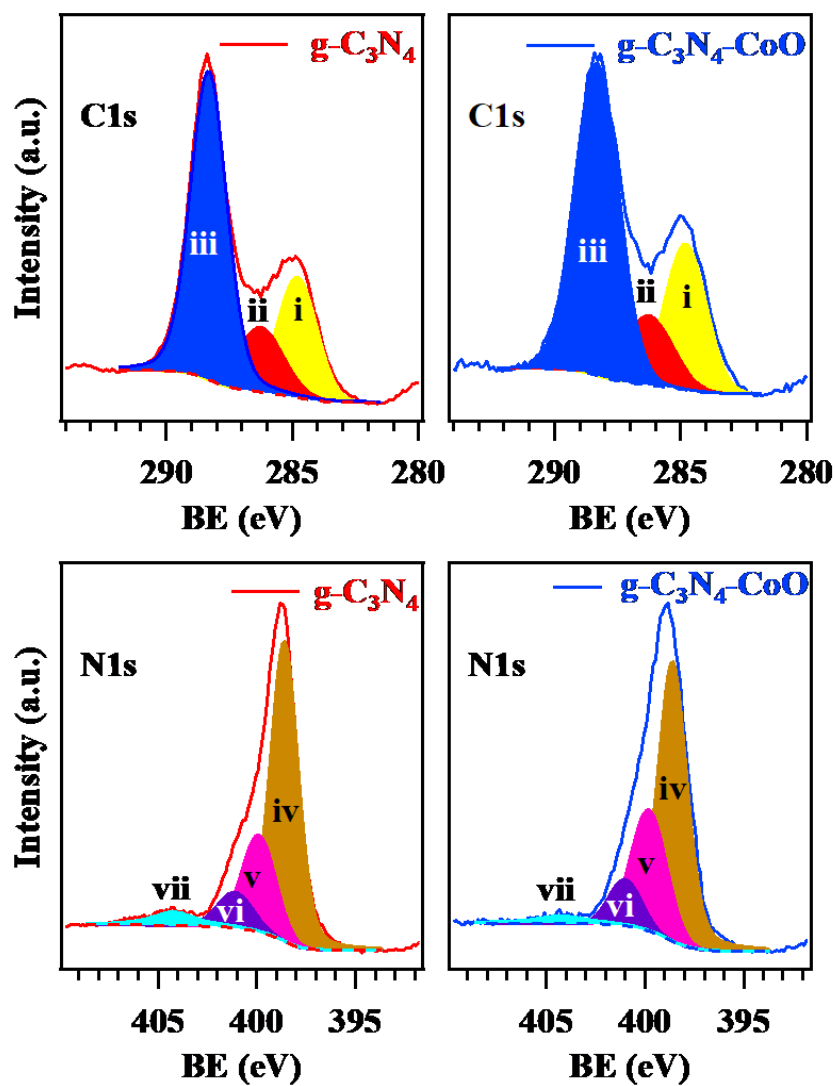
In the recorded IR spectrum (Fig. S2, right panel), the main signals related to carbon nitride could be detected. The broad band centered at  $\approx 3140 \text{ cm}^{-1}$  was due to N-H stretching vibrations of primary and secondary amino-groups, naturally occurring in the carbon nitride framework [6-7]. The bands at  $\approx 806 \text{ cm}^{-1}$  and  $1200\text{-}1600 \text{ cm}^{-1}$  were attributed to breathing modes of triazine units and to stretching modes of C-N heterocycles [4,8-9], respectively.



**Fig. S2.** Surface X-ray photoelectron spectroscopy (XPS) wide-scan spectra for the target specimens. The lack of tin signals suggested a complete coverage of the underlying FTO substrate.

sample	Atomic percentage (at.%) ratio						
	N/C	O/N	Co/N	Fe/N	O/Co	O/Fe	Co/Fe
g-C <sub>3</sub> N <sub>4</sub>	1.27	0.08	-	-	-	-	
g-C <sub>3</sub> N <sub>4</sub> -CoO	1.20	0.31	0.09	-	3.55	-	
g-C <sub>3</sub> N <sub>4</sub> -CoFe <sub>2</sub> O <sub>4</sub>	1.11	0.34	0.07	0.14	4.72	2.39	0.5

**Table S1.** Quantitative data obtained by XPS surface analyses. Calculation was carried out excluding the adventitious carbon component (see band i, Table S2). For g-C<sub>3</sub>N<sub>4</sub>-CoO and g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub> samples, both O/N and Co/N atomic percentage ratios turned out to be comparable.



**Fig. S3.** Surface C1s and N1s photoelectron peaks for bare and CoO-functionalized carbon nitride samples. Color codes and peak labeling are the same as in Figs. 2a-c in the main paper text.

sample	%		
	i	ii	iii
<b>g-C<sub>3</sub>N<sub>4</sub></b>	23.2	15.4	61.4
<b>g-C<sub>3</sub>N<sub>4</sub>-CoO</b>	25.4	15.1	59.5
<b>g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub></b>	28.9	14.7	56.4

**Table S2.** Percentage contribution of the various C1s components to the overall C1s signal for the investigated specimens. Peak labeling is the same as in Fig. 2a in the main paper text.

Sample	%			
	iv	v	vi	vii
<b>g-C<sub>3</sub>N<sub>4</sub></b>	63.6	23.9	8.5	4.0
<b>g-C<sub>3</sub>N<sub>4</sub>-CoO</b>	59.6	27.5	9.2	3.7
<b>g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub></b>	58.7	27.9	9.7	3.7

**Table S3.** Percentage contribution of the different N1s components to the overall N1s signal for the investigated specimens. Peak labeling is the same as in Fig. 2b in the main paper text.

The O1s signals presented different spectral features for the analyzed samples (Fig. S4). For bare carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), the O1s peak was dominated by component (ix) (BE= 531.9 eV), ascribable to -OH groups chemisorbed into nitrogen vacancies [4,10-14] and confirming the formation of defective carbon nitride systems (see also the observations related to the N1s photopeak in the main paper text). Functionalized specimens (g-C<sub>3</sub>N<sub>4</sub>-CoO and g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub>) displayed an additional band (viii) at BE = 529.9 eV, attributable to lattice oxygen in CoO and CoFe<sub>2</sub>O<sub>4</sub> [14-23], but band (ix) was always the predominant one (Table S4), suggesting thus the formation of highly defective systems.

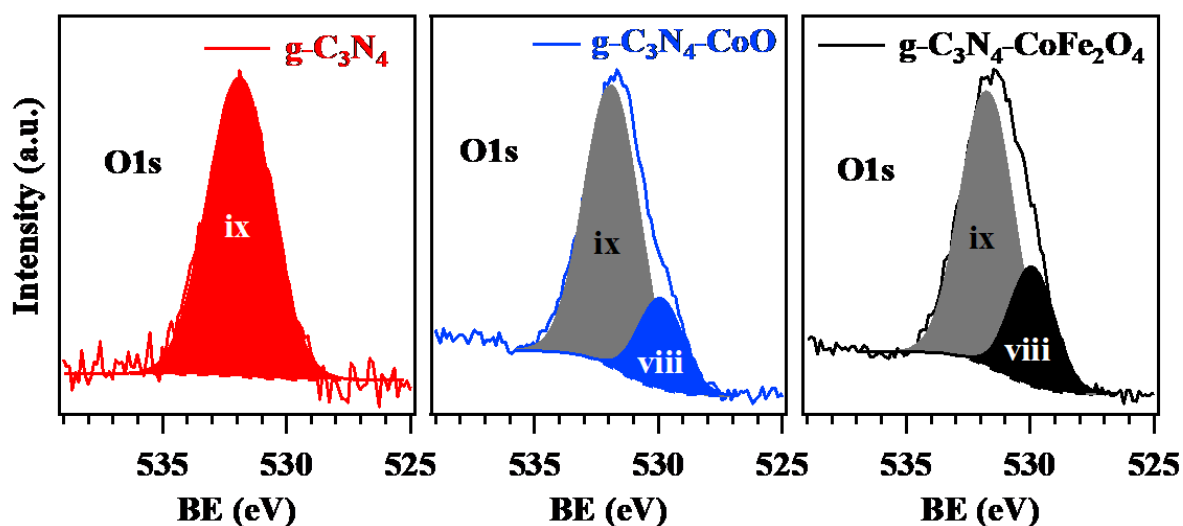
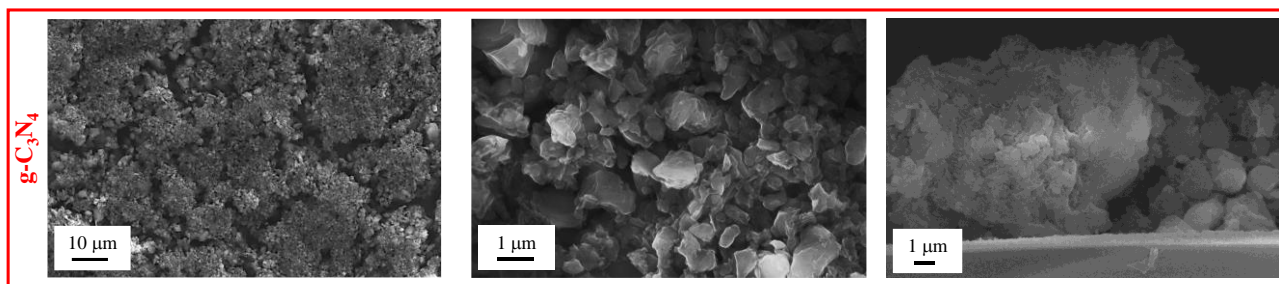


Fig. S4. Surface O1s signals for bare and functionalized carbon nitride samples.

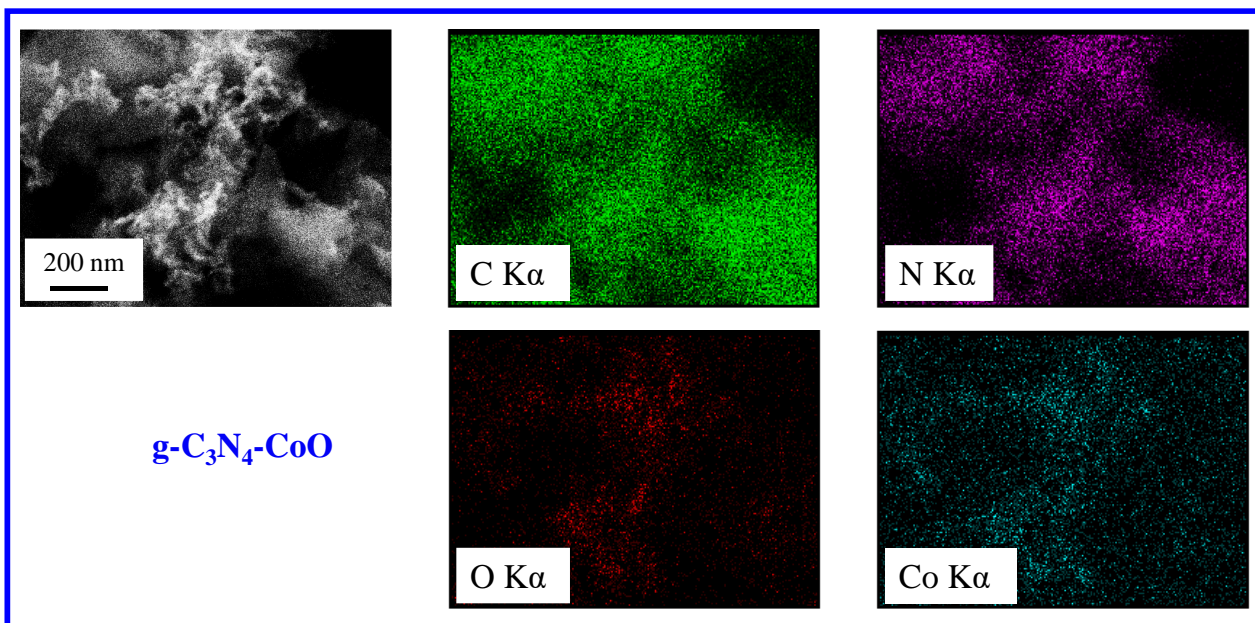
Sample	O at. %	%	
		viii	ix
g-C <sub>3</sub> N <sub>4</sub>	4.0	//	100
g-C <sub>3</sub> N <sub>4</sub> -CoO	14.0	20.7	79.3
g-C <sub>3</sub> N <sub>4</sub> -CoFe <sub>2</sub> O <sub>4</sub>	14.3	26.8	73.2

Table S4. Oxygen at.%, calculated excluding the C1s contribution from adventitious carbon (band i, Table S2), and percentage contribution of the O1s components to the overall O1s photopeak for the analyzed samples.

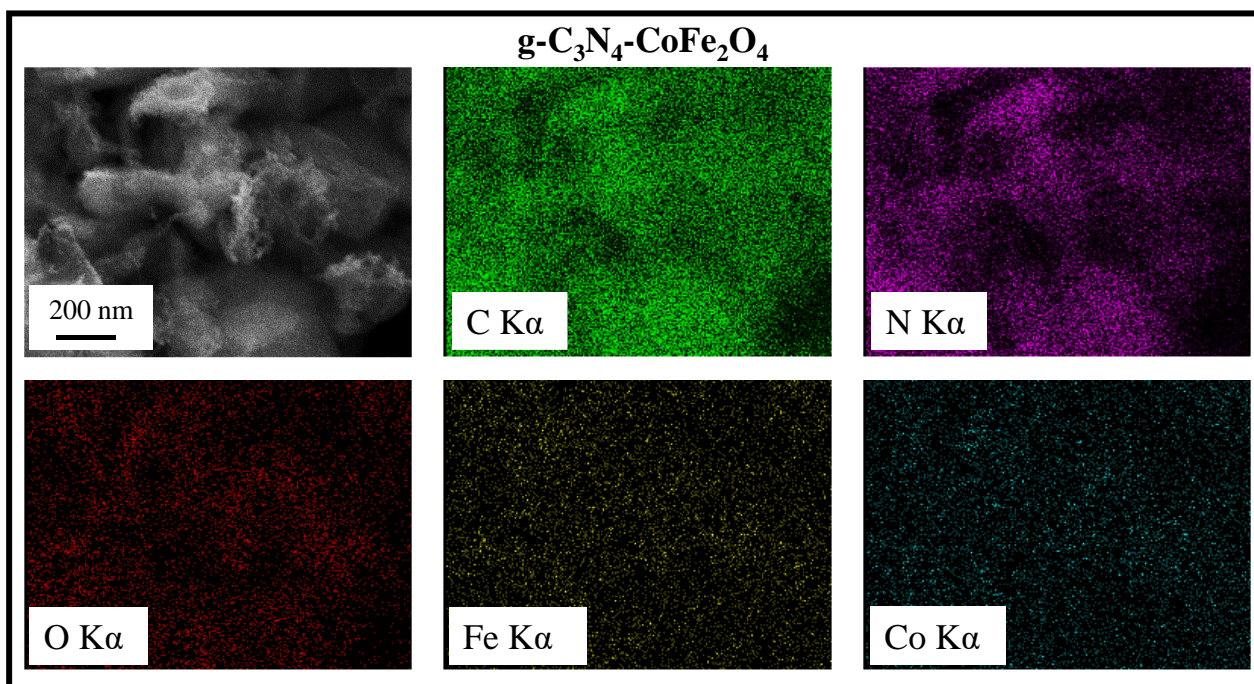




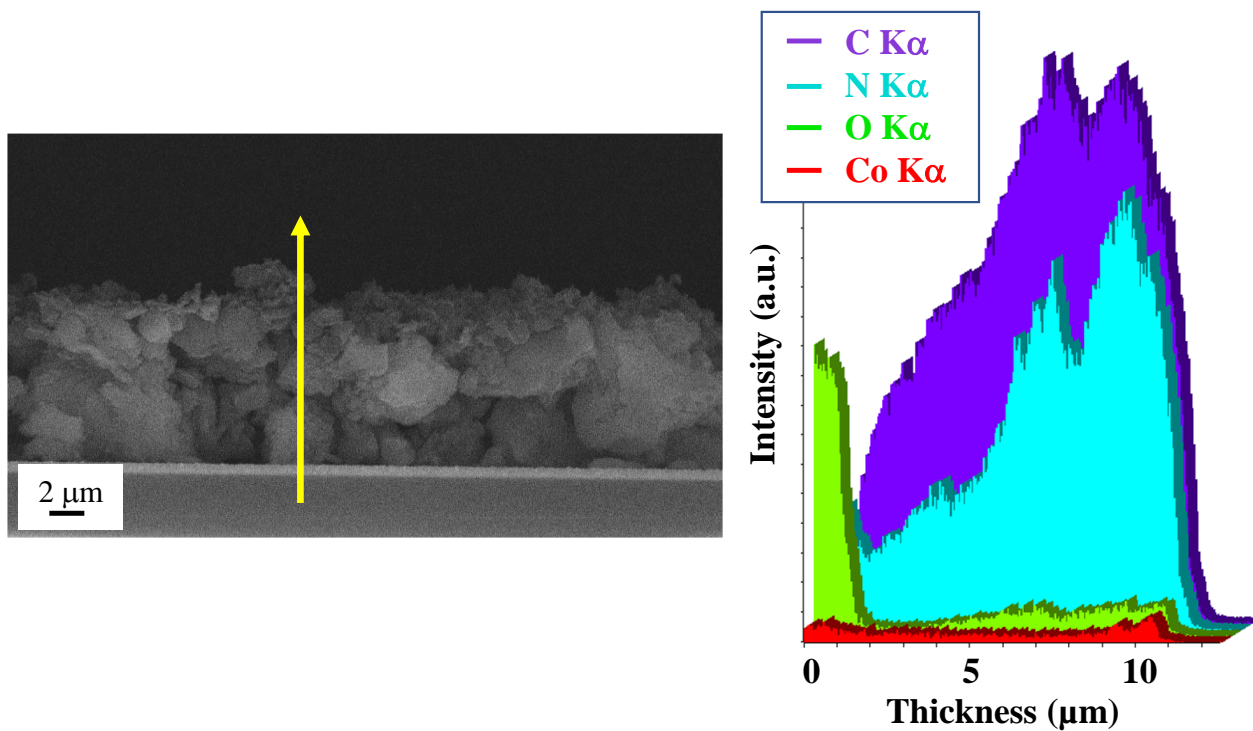
**Fig. S5.** Plane-view and cross-sectional FE-SEM images for a bare carbon nitride specimen.



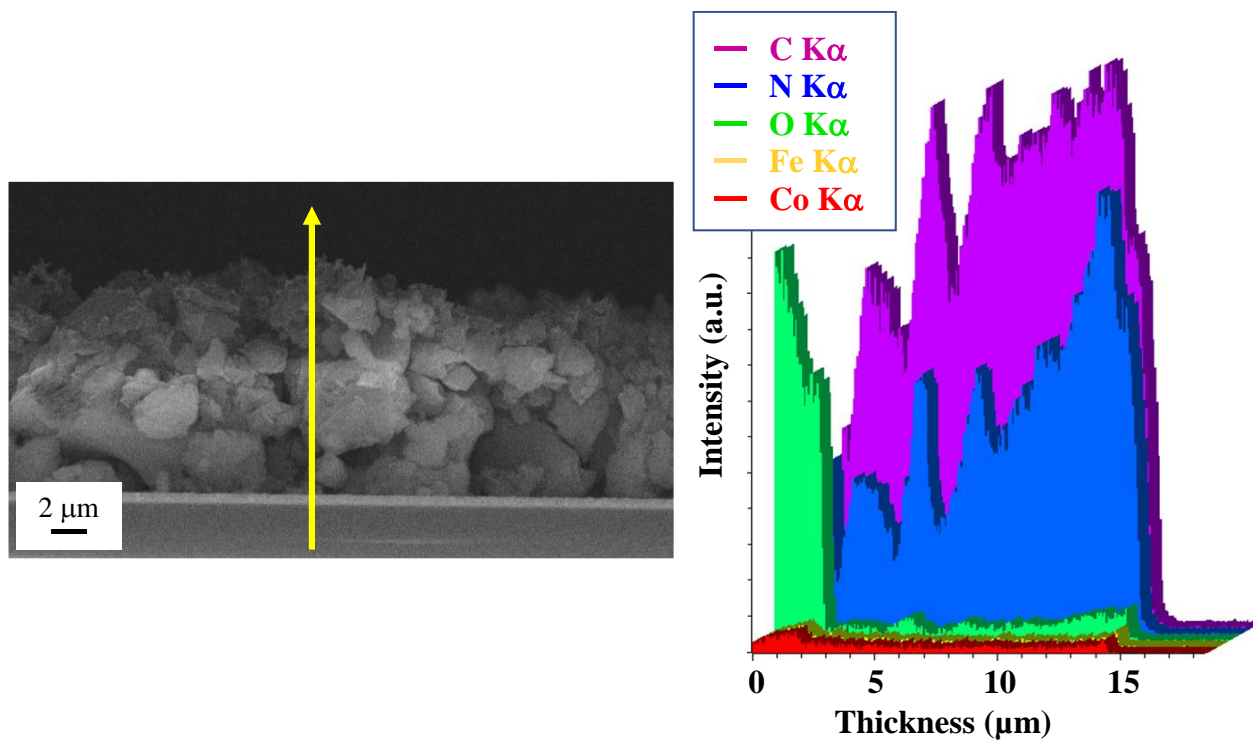
**Fig. S6.** C, N, O and Co EDXS elemental maps, recorded on the corresponding FE-SEM image, for a  $g\text{-C}_3\text{N}_4\text{-CoO}$  sample.



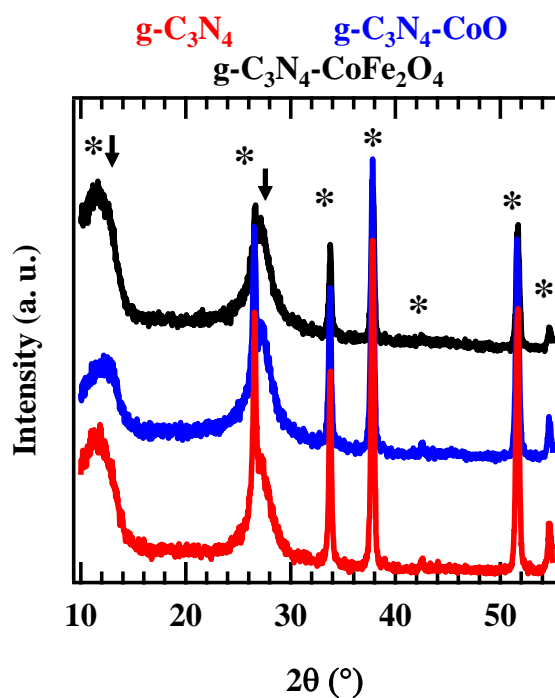
**Fig. S7.** C, N, O, Fe and Co EDXS elemental maps, recorded on the corresponding FE-SEM image, for a  $g\text{-C}_3\text{N}_4\text{-CoFe}_2\text{O}_4$  specimen.



**Fig. S8.** EDXS cross-sectional line scan data for  $g\text{-C}_3\text{N}_4\text{-CoO}$ , recorded along the yellow line marked in the reported FE-SEM image. Arrow indicates the direction of abscissa increase.



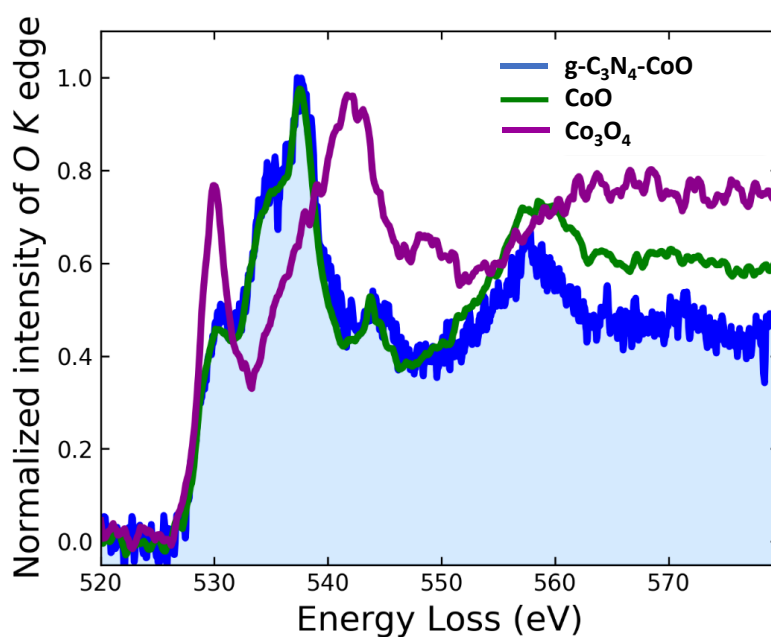
**Fig. S9.** EDXS cross-sectional line scan data for  $g\text{-C}_3\text{N}_4\text{-CoFe}_2\text{O}_4$ , recorded along the yellow line marked in the reported FE-SEM image. Arrow indicates the direction of abscissa increase.



**Fig. S10.** XRD patterns recorded in glancing incidence mode ( $\theta_i = 1.0^\circ$ ) for bare and functionalized carbon nitride samples supported on FTO. Stars (\*) indicate reflections attributed to the FTO-coated glass substrate, whereas arrows mark the peak positions for graphitic carbon nitride.

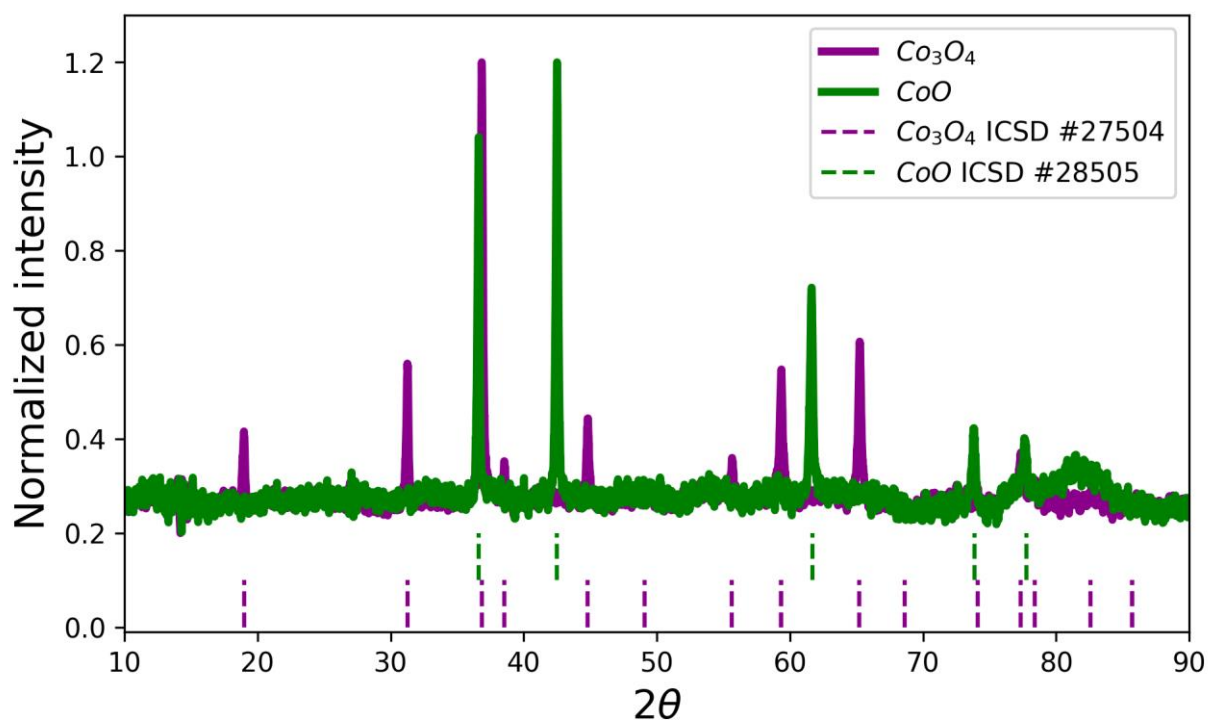
XRD patterns of the target specimens (Fig. S10) were characterized by two relatively broad signals located at  $2\theta = 13.1^\circ$  and  $27.2^\circ$ , both partially overlapped with intense reflections pertaining to the FTO substrate. The former is associated with the packing of tri-s-triazine units ((100) diffraction plane [24]), whereas the latter is related to the (002) plane corresponding to the interplanar stacking of carbon nitride sheets [25]. The lack of clearly detectable signals ascribable to cobalt/iron oxides was mainly traced back to their low amount and high dispersion [26], as confirmed by TEM and XPS analyses.

Chemical composition of the samples was verified by EELS. As a reference for the experimental data from g-C<sub>3</sub>N<sub>4</sub>-CoO sample, CoO and Co<sub>3</sub>O<sub>4</sub> powders with known composition were measured using XRD and EELS. Fig S11 reports a comparison of the O K edges of g-C<sub>3</sub>N<sub>4</sub>-CoO with reference samples confirming the CoO phase.

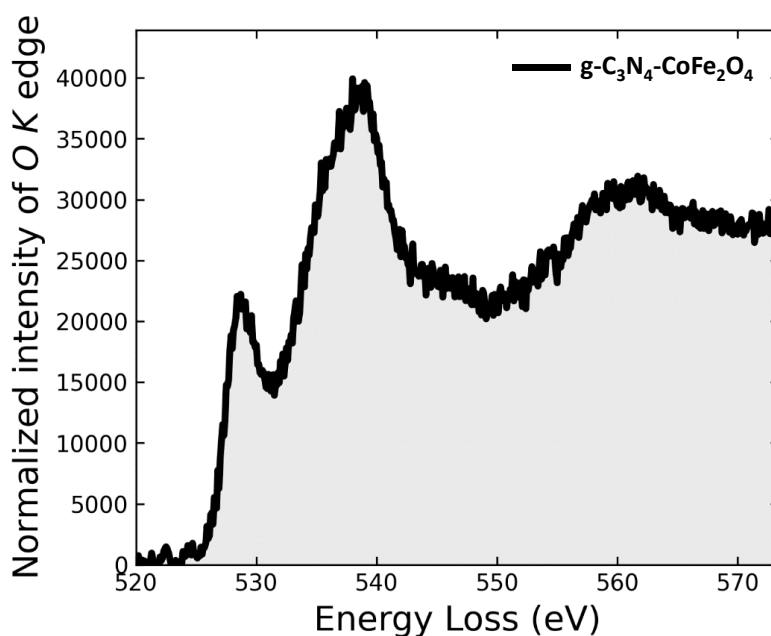


**Fig. S11.** EELS spectra of the O K edge acquired on g-C<sub>3</sub>N<sub>4</sub>-CoO (blue), compared with reference spectra taken on CoO (green) and Co<sub>3</sub>O<sub>4</sub> (purple) commercial powders.

Fig. S12 presents experimental XRD patterns of CoO and Co<sub>3</sub>O<sub>4</sub> powders, showing good agreement with ICSD data 28505 and 27504, respectively. Fig. S13 shows O K edge of g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub> sample.



**Fig. S12.** XRD patterns of CoO (green) and Co<sub>3</sub>O<sub>4</sub> (purple) reference powder samples. The dashed vertical lines mark peak positions corresponding to the reported ICSD cards.

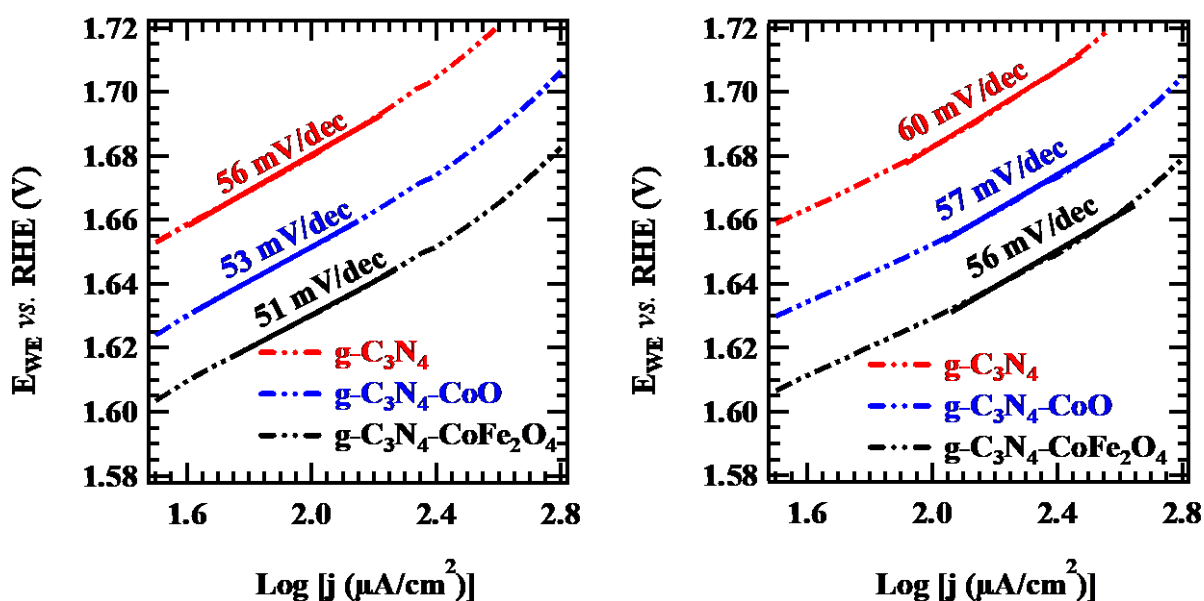


**Fig. S13.** EELS spectrum of the O K edge for g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub> specimen.

§ S3. Photoelectrochemical tests

Material	$j_{1.23}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{onset}}$ ( $\text{V}_{\text{RHE}}$ )	$\text{ABPE}_{\text{max}}$	$E_{\text{Wmax}}$ ( $\text{V}_{\text{RHE}}$ )
g-C <sub>3</sub> N <sub>4</sub>	1.98	1.12	1	1.12
g-C <sub>3</sub> N <sub>4</sub> -CoO	3.32	1.08	2.31	1.13
g-C <sub>3</sub> N <sub>4</sub> -CoFe <sub>2</sub> O <sub>4</sub>	3.60	1.06	2.47	1.10

**Table S5.** Summary of representative photoelectrochemical analysis results. Comparison of photocurrent densities at  $E = 1.23$  V ( $j_{1.23}$ ) vs. the reversible hydrogen electrode (RHE), onset potential ( $E_{\text{onset}}$ , calculated at  $1 \mu\text{A}/\text{cm}^2$ ), relative applied bias photon-to-current efficiency maximum ( $\text{ABPE}_{\text{max}}$ ) normalized with respect to the bare g-C<sub>3</sub>N<sub>4</sub> specimen, and potential of maximum efficiency ( $E_{\text{Wmax}}$ , corresponding to the maximum in ABPE curves).



**Fig. S14.** Tafel plots for bare and functionalized carbon nitride electrodes, under illumination (left) and in the dark (right). Dashed and continuous lines indicate experimental and fitting curves, respectively.

<b>LIGHT</b>				
<b>Material</b>	<b>Electrolyte</b>	<b>j @ 1.55 V (<math>\mu\text{A}/\text{cm}^2</math>)</b>	<b>Tafel slope (mV/decade)</b>	<b>Ref.</b>
<b>g-C<sub>3</sub>N<sub>4</sub></b>	KOH 0.1 M	9.4	54	Present work
<b>g-C<sub>3</sub>N<sub>4</sub>-CoO</b>		11.7	53	
<b>g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub></b>		24.5	51	
<b>DARK</b>				
<b>g-C<sub>3</sub>N<sub>4</sub></b>	KOH 0.1 M	2.6	60	Present work
<b>g-C<sub>3</sub>N<sub>4</sub>-CoO</b>		4.0	57	
<b>g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub></b>		12.5	56	

**Table S6.** OER electrochemical performances for the materials fabricated in the present work under light and dark conditions.

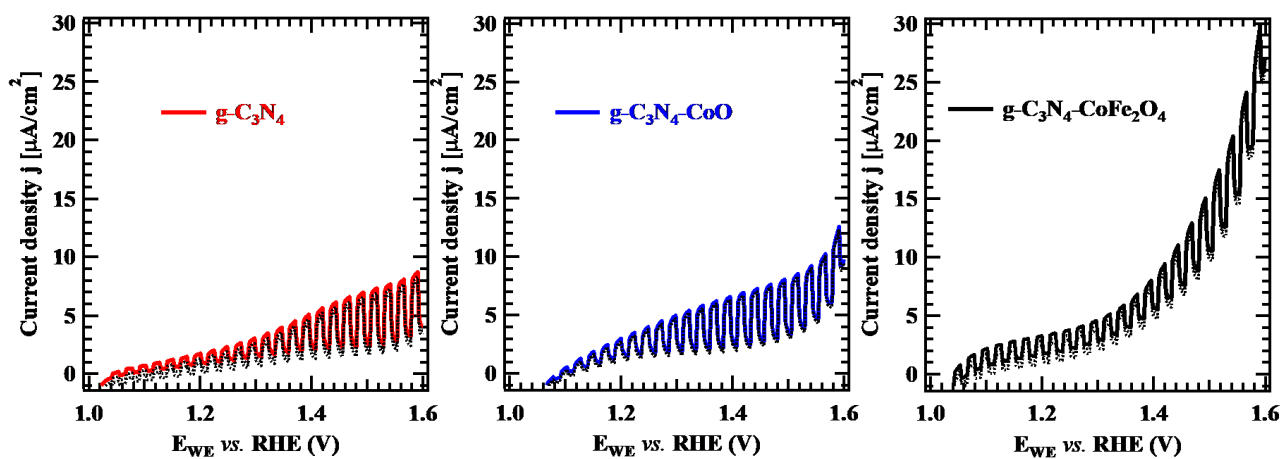


Material	Electrolyte	j @ 1.55 V ( $\mu\text{A}/\text{cm}^2$ )	Tafel slope (mV/decade)	Ref.
g-C <sub>3</sub> N <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub> 0.5 M	$\approx 0.30-0.75^a$	<i>n.a.</i>	[27]
g-C <sub>3</sub> N <sub>4</sub>		$\approx 2.2-7.2^b$	<i>n.a.</i>	
g-C <sub>3</sub> N <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub> 0.2 M	0 <sup>a</sup>	<i>n.a.</i>	[5]
g-C <sub>3</sub> N <sub>4</sub>	KOH 1.0 M	0 <sup>b</sup>	122	[28]
g-C <sub>3</sub> N <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub> 0.2 M	$\approx 12^a$	<i>n.a.</i>	[29]
g-C <sub>3</sub> N <sub>4</sub>		$\approx 15^b$	<i>n.a.</i>	
CoO <sub>x</sub> -C <sub>3</sub> N <sub>4</sub>	KOH 1.0 M	$\approx 4000^a$	74.5	[30]
Co <sub>3</sub> O <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	KOH 1.0 M	$\approx 10000^a$	67	[31]
Co <sub>3</sub> O <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub> 0.2 M	0 <sup>a</sup>	<i>n.a.</i>	[5]
Co <sup>2+</sup> - g-C <sub>3</sub> N <sub>4</sub> <sup>c</sup>	Na <sub>2</sub> SO <sub>4</sub> 0.2 M	$\approx 48^c$	<i>n.a.</i>	[29]
Co <sup>2+</sup> - g-C <sub>3</sub> N <sub>4</sub> <sup>c</sup>		$\approx 40^a$	<i>n.a.</i>	
CoFe <sub>2</sub> O <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	KOH 0.1 M	$\approx 0^a$	<i>n.a.</i>	[32]
NiFe <sub>2</sub> O <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>		$\approx 0^a$	<i>n.a.</i>	
Co-N/Co-O@N-doped C <sup>d</sup>	KOH 0.1 M	$\approx 1300-2500^a$	75.1-115.2	[33]

**Table S7.** OER performances of selected electrocatalysts based on carbon nitride systems, both as such and incorporating Co centers, or combined in composites with Co/Fe oxides. *n.a.* = not available. <sup>a</sup> dark conditions; <sup>b</sup> light conditions; <sup>c</sup> cobalt-incorporated carbon nitride films; <sup>d</sup> mixed cobalt nitride and cobalt oxide nanofragments encapsulated in thin layers of nitrogen-doped carbon nanostructure.

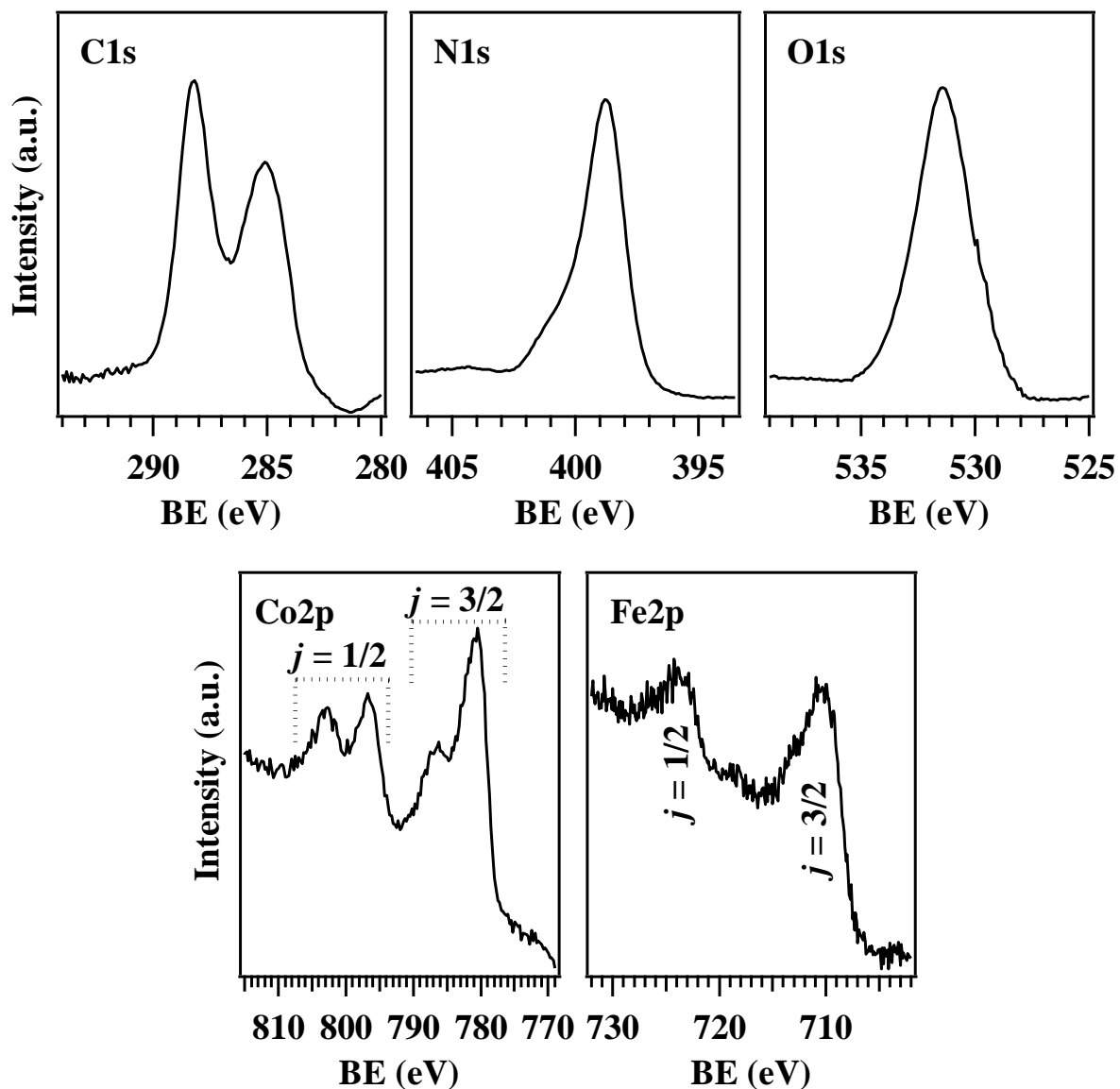
<b>Material</b>	<b>Electrolyte</b>	<b>j @ 1.55 V (<math>\mu\text{A}/\text{cm}^2</math>)</b>	<b>Tafel slope (mV/decade)</b>	<b>Ref.</b>
IrO <sub>2</sub>	KOH 1.0 M	18000	149	[34]
IrO <sub>2</sub>	KOH 1.0 M	53000	91	[35]
IrO <sub>2</sub>	KOH 0.1 M	8000	113	[36]
IrO <sub>2</sub>	KOH 1.0 M	27000	67	[37]
RuO <sub>2</sub>		15000	89	
RuO <sub>2</sub>	KOH 0.1 M	17000	71	[38]
RuO <sub>2</sub>	KOH 1.0 M	13000	74	[39]

**Table S8.** OER performances of selected IrO<sub>2</sub> and RuO<sub>2</sub> electrocatalysts under dark conditions.

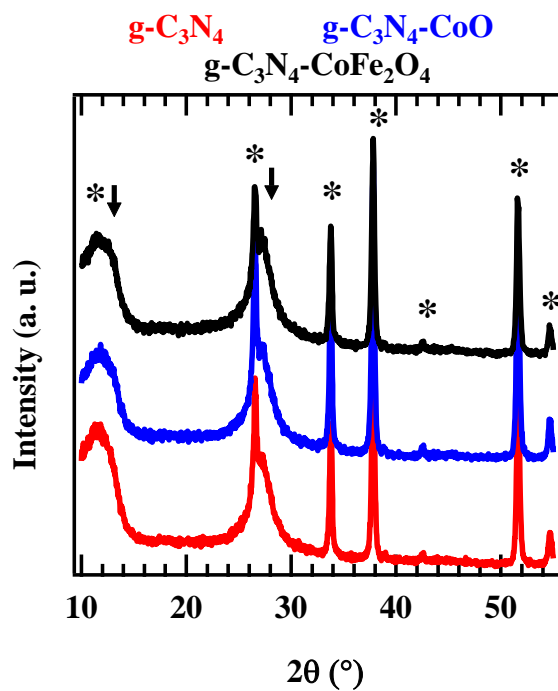


**Fig. S15.** Linear sweep voltammetry (LSV) curves collected on as-prepared samples (solid lines) and recorded every 90 days over a period of six months (dashed lines).

§ S-4. Chemico-physical characterization after photoelectrochemical tests



**Fig. S16.** XPS analysis for g-C<sub>3</sub>N<sub>4</sub>-CoFe<sub>2</sub>O<sub>4</sub> after storage under ambient conditions for six months, during which the sample was photoelectrochemically tested every 90 days.



**Fig. S17.** XRD patterns collected in glancing incidence mode ( $\theta_i = 1.0^{\circ}$ ) after storing the investigated specimens under ambient conditions for six months, during which the samples were photoelectrochemically tested every 90 days. Stars (\*) mark reflections attributed to the FTO-coated glass substrate, whereas arrows indicate the peak positions for graphitic carbon nitride.

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