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

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Abstract

The ever-increasing energy demand from the world population has made the intensive use of fossil fuels an overarching threat to global environment and human health. An appealing alternative is offered by sunlight-assisted photoelectrochemical water splitting to yield carbon-free hydrogen fuel, but kinetic limitations associated to the oxygen evolution reaction (OER) render the development of cost-effective, eco-friendly and stable electrocatalysts an imperative issue. In the present work, OER catalysts based on graphitic carbon nitride (g-C₃N₄) were deposited on conducting glass substrates by a simple decantation procedure, followed by functionalization with low amounts of nanostructured CoO and CoFe₂O₄ by radio frequency (RF)-sputtering, and final annealing under inert atmosphere. A combination of advanced characterization tools was used to investigate the interplay between material features and electrochemical performances. The obtained results highlighted the formation of a *p-n* junction for the g-C₃N₄-CoO system, whereas a *Z*-scheme junction accounted for the remarkable performance enhancement yielded by g-C₃N₄-CoFe₂O₄. The intimate contact between the system components also afforded an improved electrocatalyst stability in comparison to various bare and functionalized g-C₃N₄-based systems. These findings emphasize the importance of tailoring g-C₃N₄ chemico-physical properties through the dispersion of complementary catalysts to fully exploit its applicative potential.

Keywords: CoO; CoFe₂O₄; graphitic carbon nitride; RF-sputtering; oxygen evolution reaction.

1. Introduction

The ever-increasing overreliance on the burning of non-renewable fossil fuels and the consequent detrimental greenhouse gases emission have stimulated the exploration of green energy alternatives to suppress global warming and environmental pollution [1-2]. In this context, an urgent need highlighted by the Intergovernmental Panel on Climate Change (IPCC) is to decarbonize the current energy portfolio to a cleaner and more sustainable one [3-4], as promised by the transition to a hydrogen-based economy. In fact, molecular hydrogen (H_2) stands as an attractive energy vector thanks to its high energy density ($\approx 142 \text{ MJ} \times \text{kg}^{-1}$) and carbon-free nature [5-6]. The abundant sunlight, a renewable and inexhaustible natural resource reaching the Earth surface ($1.3 \times 10^5 \text{ TW}$ per year), provides a valuable means for a sustainable production of H_2 , which, to date, is mainly obtained on an industrial scale by energy-intensive steam reforming [7]. In particular, photoelectrochemical water splitting into O_2 and H_2 features a remarkable applicative potential towards a clean and large-scale hydrogen generation [8-10]. Nonetheless, the overall process efficiency is limited by the kinetic limitations associated to the oxygen evolution reaction (OER) [8,10-12], the bottleneck of water splitting. To date, noble metal oxides (IrO_2 and RuO_2) are regarded as the OER benchmark catalysts, but their large-scale application is precluded by their high cost, environmental footprint and supply shortage [11,13-14]. As a consequence, the development and implementation of cost-effective and highly active and stable OER catalysts based on earth-abundant and eco-friendly elements is highly demanded for a commercially viable H_2 generation without any significant harm on environment and human health.

In the actual tide of possible candidates, graphitic carbon nitride ($g\text{-}C_3N_4$), a cost-effective and metal-free semiconductor, presents a range of superior properties if compared to other possible systems. These include its high thermal and physico-chemical stability in basic/acidic media, amenable reactivity, suitable band edges for water splitting, tuneable electronic structure, and band gap enabling Vis light harvesting ($E_G \approx 2.7 \text{ eV}$) [1,15-22]. It is worthwhile highlighting

that g-C₃N₄ consists of earth-abundant and non-toxic elements, a feature rendering it a very attractive alternative for real-world applications in comparison to widely used metal oxide-containing OER electrocatalysts, to reduce the environmental footprint and improve the process sustainability. As a consequence, over the last decade g-C₃N₄ systems have been the subject of a huge number of research works worldwide. Nevertheless, the above mentioned advantages are partially eclipsed by the low active area, limited amount of active sites, and relatively rapid electron-hole recombination [23-24]. To this regard, two successful strategies to enhance bare g-C₃N₄ activity are based on the tailoring of its nano-organization and on its combination with transition metal oxide complementary catalysts [15,25-27]. The latter option is, in principle, highly appealing not only to improve g-C₃N₄ absorption, but also to enhance charge carrier separation through the construction of suitable semiconductor heterojunctions. A careful choice of the system components and the implementation of versatile preparation routes, which, in turn, directly influence the nature of the established material junctions [28], open broad perspectives to modulate and boost functional performances in view of possible large-scale end-uses [16,26,29].

In this work, we present an amenable and innovative fabrication route to supported OER photoelectrocatalysts based on the combination of g-C₃N₄ with single and multi-metal transition metal oxide nanoparticles. In particular, CoO and CoFe₂O₄ have been chosen as functional activators due to their inherent catalytic activity in different oxidation reactions, enabling an improvement of bare g-C₃N₄ behavior in various photo-assisted processes, including water oxidation [18,29-31]. Up to date, composite systems combining g-C₃N₄ with CoO and CoFe₂O₄ have been mainly prepared by wet synthetic procedures for electrochemical supercapacitors [32] and photocatalysts for pollutant degradation [17-18,33-36], and some studies have focused on their use in H₂O splitting [16,30,37]. To the best of our knowledge, so far the target materials have been mainly investigated in a powdered form [16-18,21,33-36], whereas only few contributions have been dedicated to supported systems [30,32,37-38], which are highly required for a practical

integration in real-world end-uses.

Herein, g-C₃N₄ deposits were prepared on conductive glass substrates by a simple and cost-effective decantation procedure, involving the use of pre-synthesized C₃N₄ powders obtained by thermal condensation of melamine. Subsequently, g-C₃N₄ deposits were functionalized with ultra-dispersed CoO and CoFe₂O₄ nanoparticles *via* radio frequency (RF)-sputtering from non-equilibrium plasmas (see Fig. 1). The main advantages of the adopted preparation route, which, to our knowledge, has never been employed before for the preparation of the target materials, are related to the inherent sputtering infiltration power and the possibility of achieving a controlled

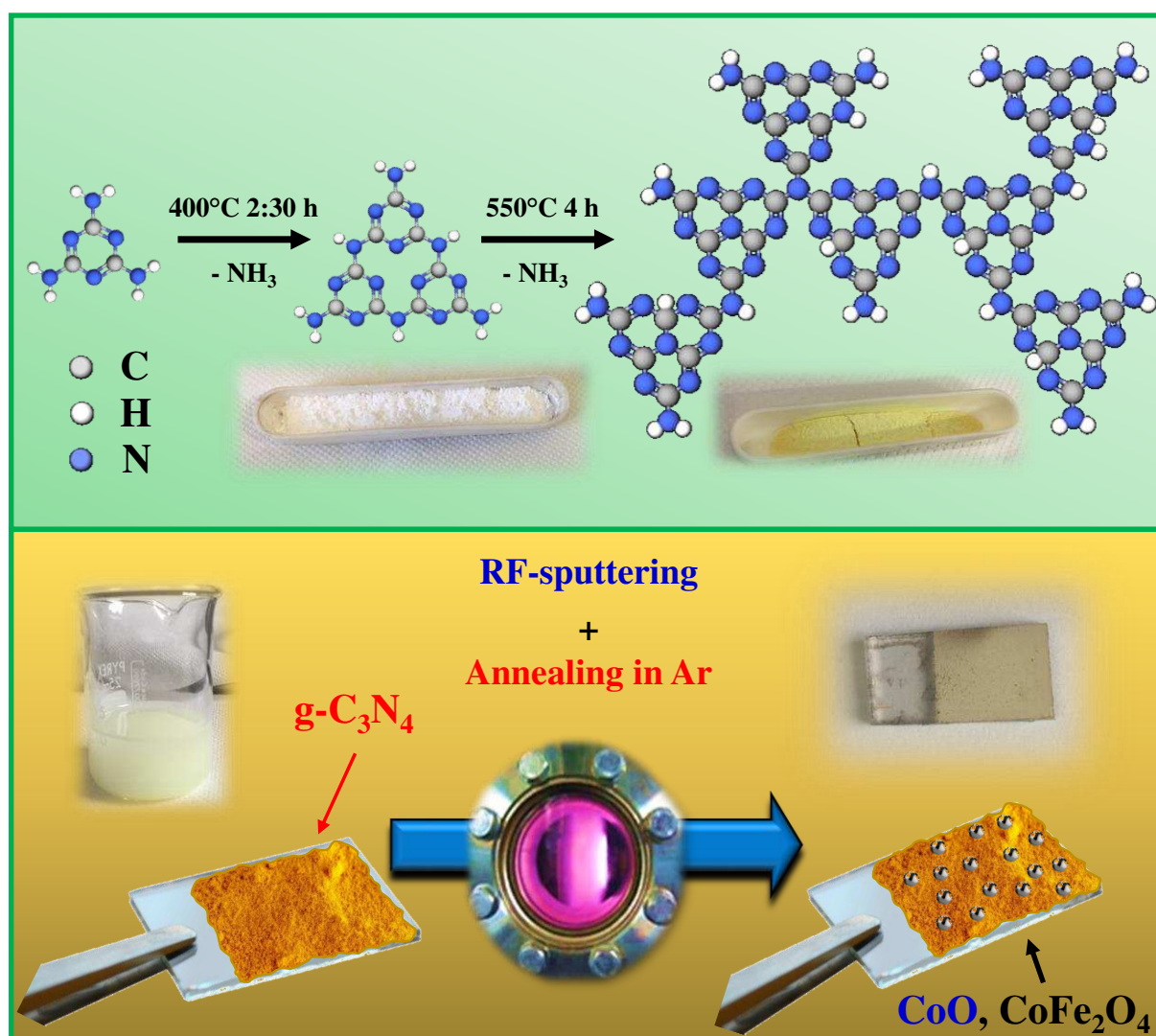


Fig. 1. Sketch of the fabrication procedure adopted in the present work for carbon nitride (g-C₃N₄)-based electrodes functionalized with CoO (g-C₃N₄-CoO) and CoFe₂O₄ (g-C₃N₄-CoFe₂O₄).

g-C₃N₄ functionalization under mild operational conditions. The resulting intimate contact between the system components is of key importance in order to favorably exploit their mutual chemical/electronic interactions, ultimately leading to enhanced functional performances. In particular, the functionalization of g-C₃N₄ with CoO [16,23,29,35,39], and especially with CoFe₂O₄ [17-18,33,38], resulted in the tailored formation of carbon nitride/metal oxide heterojunctions. Photoelectrochemical tests enabled to attain a valuable insight into the nature of these junctions (CoO/g-C₃N₄ or CoFe₂O₄/g-C₃N₄) and their efficiency in the Vis light-production of electron/hole pairs, with particular regard to the enhancement of hole concentration on oxide nanoparticles in contact with the reaction medium. As a result, the target systems, and especially g-C₃N₄-CoFe₂O₄, featured an attractive photoactivity increase in comparison to the pristine g-C₃N₄ in the proximity of H₂O thermodynamic oxidation potential. In addition, the developed materials yielded a favorable operational stability in comparison to various g-C₃N₄-based electrocatalysts, an important figure of merit for real-world end-uses. In this study, the origins of performance boosting brought about by g-C₃N₄ functionalization are presented and critically discussed basing on the outcomes of a multi-technique characterization, which enabled to elucidate the interplay between material structure, composition, nano-organization and photoelectrochemical performances. The obtained results may act as a useful guide for further implementation of highly active, economically viable and stable OER photoanodes aimed at solar hydrogen production.

2. Experimental section

2.1 Material synthesis

The deposition of g-C₃N₄ on fluorine-doped tin oxide (FTO)-coated glass substrates was accomplished by a decantation procedure. In particular, pre-grinded carbon nitride powders (16 mg), synthesized as reported in the Supporting Information (SI; see also Fig. S1) were

preliminarily suspended in 8 mL isopropanol and sonicated for 1 h. The suspension was transferred into a beaker, in which a suitably pre-cleaned FTO glass slide (Aldrich®; $\approx 7 \Omega \times \text{sq}^{-1}$; FTO layer thickness $\approx 600 \text{ nm}$) was laid on the bottom for 24 h. The resulting deposit was dried in air for 15 min before undergoing annealing in an Ar atmosphere (500°C for 2.5 h; heating rate = $3^\circ\text{C}/\text{min}$).

g-C₃N₄ deposits functionalization was performed by RF-sputtering from weakly ionized Ar plasmas (purity = 5.0), using a two-electrode custom-built plasmochemical reactor ($\nu = 13.56 \text{ MHz}$). Co (Alfa Aesar®; thickness = 0.25 mm; purity = 99.95%; diameter = 5 cm) or Co₃O₄-Fe₂O₃ targets (Neyco; thickness = 2 mm; purity = 99.9%; $50 \times 50 \text{ mm}^2$) were fixed on the RF-electrode, whereas FTO-supported g-C₃N₄ specimens were mounted on the grounded one. Hereafter, the obtained functionalized systems are indicated as g-C₃N₄-A, where A = CoO or CoFe₂O₄. Basing on previous results [40], depositions were performed using the following optimized experimental settings: RF-power = 20 W; growth temperature = 60°C ; Ar flow rate = 10 standard cubic centimeters per minute (sccm); total pressure = 0.3 mbar; process duration = 180 and 195 min for g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄, respectively. All the resulting materials were finally annealed in Ar atmospheres (500°C , 2.5 h; heating rate = $3^\circ\text{C}/\text{min}$).

2.2 Material characterization

X-ray photoelectron (XPS) analyses were carried out on a Perkin-Elmer Φ 5600-ci instrument at a pressure $< 10^{-8}$ mbar using a non-monochromatized Mg K α excitation ($h\nu = 1253.6 \text{ eV}$), to avoid the overlap of Co and Fe Auger peaks with Fe2p and Co2p ones, respectively, occurring with the standard Al K α X-ray source [10]. No sputtering was carried out. Binding energy (BE) values were corrected for charging effects by assigning a value of 284.8 eV to the adventitious C1s signal [41]. After a Shirley-type background subtraction, peak fitting was carried out by the XPSPEAK software (accessed June, 2022 [42]). Atomic percentages (at. %) were

calculated by peak area integration using Φ V5.4A sensitivity factors. Field emission-scanning electron microscopy (FE-SEM) analyses were performed using a Zeiss SUPRA 40VP instrument, at primary beam acceleration voltages of 10–20 kV. Selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDXS) analyses were carried-out on a ThermoFisher Scientific Osiris microscope equipped with a Super-X windowless EDX detector system operated at 200 kV. High-resolution electron energy loss spectroscopy (EELS) data were recorded using a state-of-the-art double-corrected and monochromated Thermo Fisher Scientific Titan³ 80-300 microscope operated at 120 kV (energy resolution = 120 meV; convergence and collection angle = 19 and 90 mrad, respectively). Spectra were acquired on a Direct detection Gatan K2 camera mounted on a GIF Quantum spectrometer (0.2 s/pixel). Reference spectra on CoO and Co₃O₄ were acquired with a dispersion of 0.1 eV/pixel, whereas spectra for g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄ were acquired with a dispersion of 0.05 eV/pixel. Energy calibration issues were corrected by aligning the experimental spectrum to the reference one, and the dispersion of the g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄ spectra was found to be 0.0505 eV/pixel. High-resolution scanning transmission electron microscopy (STEM) images were acquired at 300 kV acceleration voltage using 50 pA probe current, a convergence semi-angle of 21 mrad, and collection angles of 29-160 mrad [high angle annular dark field (HAADF) imaging] and 0-20 mrad [bright field (BF) imaging]. Optical absorption spectra were registered operating in diffuse reflectance mode by a Cary 50 (Varian) dual-beam spectrophotometer (spectral bandwidth = 1 nm). Band gap (E_G) evaluation was performed using the Tauc equation $[f(R)hv]^n$ vs. hv , where $f(R)$ is the Kubelka-Munk function and R is the measured reflectance, assuming the occurrence of allowed indirect transitions ($n = 1/2$) [12,18,39].

2.3 Photoelectrochemical tests

Photoelectrochemical measurements were carried out at room temperature using an

electrochemical working station (Autolab PGSTAT204 potentiostat/galvanostat) and a three-electrode set-up. The FTO-supported materials were employed as working electrodes (WEs), while a Pt coil was used as counterelectrode (CE). A standard calomel electrode [SCE; $E_{SCE} = 0.256$ V *vs.* the reversible hydrogen electrode (RHE)] was employed as reference electrode (RE). Prior to measurements, samples were cycled between 1.0 and 1.8 V *vs.* RHE, until a constant behavior was obtained. During a typical test, the WE was illuminated on the front side (electrode-electrolyte interface, EE illumination) using a white light LED source. A 0.1 M KOH solution (pH = 12.9) was used as the electrolyte. The potential *vs.* SCE (E_{SCE}) was converted into the RHE scale using the formula:

$$E_{RHE} = E_{WE} (V) + E_{SCE} (V) + 0.0592 \cdot \text{pH} \quad (1)$$

where E_{WE} represents the bias applied to the working electrode. Linear sweep voltammetry (LSV) curves were collected at a scan rate of 5 mV s⁻¹. Current density (*j*) values were obtained by normalizing the measured currents for the exposed geometric area (0.283 cm²). Chronoamperometry (CA) analyses were performed at 1.5 V *vs.* RHE.

Applied bias photon-to-current efficiency (ABPE) curves were derived from photocurrent density *vs.* bias data through the following equation [43]:

$$\text{ABPE} (\%) = ([j \times (1.23 - E_{RHE})] / P) \times 100 \quad (2)$$

where *j* (mA×cm⁻²) is the photocurrent density at a given applied potential (E_{RHE}) and *P* is the incident light intensity (≈150 mW×cm⁻²).

Further details on material synthesis and characterization are reported in the SI.

3. Results and discussion

3.1 Material characterization

The surface chemical composition was investigated by XPS, a fundamental analytical tool

to investigate the elemental chemical environments in g-C₃N₄-based materials [44]. Wide-scan spectra (Fig. S2) revealed the presence of C and N photopeaks, as expected. For functionalized specimens, even the occurrence of cobalt (g-C₃N₄-CoO), or cobalt and iron (g-C₃N₄-CoFe₂O₄) photoelectron and Auger signals could be clearly discerned, suggesting a dispersion of functionalizing agents over the underlying carbon nitride, with no complete coverage of the latter. Quantitative analyses (Table S1) indicated an increase in the oxygen content upon going from bare carbon nitride (g-C₃N₄) to functionalized specimens (g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄), pointing out the occurrence of Co and Fe in oxidized forms. The average N/C at.% ratio of (1.20±0.08) (see Table S1), slightly lower than the value for stoichiometric g-C₃N₄ (1.33), suggested the presence of nitrogen deficiencies. The latter, whose role in carbon nitride-based photocatalysts is rarely considered, can play a key role in modifying photoactivated material performances [45]. In order to achieve a deeper insight into the elemental chemical environments, narrow scan C1s and N1s photopeaks were recorded and deconvoluted. As can be observed in Fig. 2a and S3 (compare also Table S2), irrespective of the specific sample, three different components contributed to the overall C1s signal (see Fig. 2c for a detailed assignment): **i**) adventitious carbon contamination (BE = 284.8 eV) [46-48]; **ii**) carbon bonded to amino groups (C-NH_x, x = 1, 2) on g-C₃N₄ heptazine ring edges (average BE = 286.2 eV) [12,49]; **iii**), the predominant contribution, due to N-C=N carbon atoms in the aromatic rings of g-C₃N₄ framework (mean BE = 288.3 eV) [16,35,39,46,50]. At variance with previous studies [48], no appreciable bands related to C-O moieties could be observed.

For all samples, the N1s signal could be deconvoluted by means of the following four bands (Fig. 2b and S3; see also Fig. 2c): **iv**), the main one (average BE = 398.6 eV), attributable to bi-coordinated nitrogen centers (C=N-C) [51-54]; **v**), with an average BE of 399.8 eV, ascribed to tri-coordinated N atoms [N-(C)₃] in the g-C₃N₄ structure [44,46,49-50,52]; **vi**), related to NH_x (x = 1, 2) groups in the heptazine framework (average BE = 401.0 eV) [44,47-48,50,53,55]; **vii**),

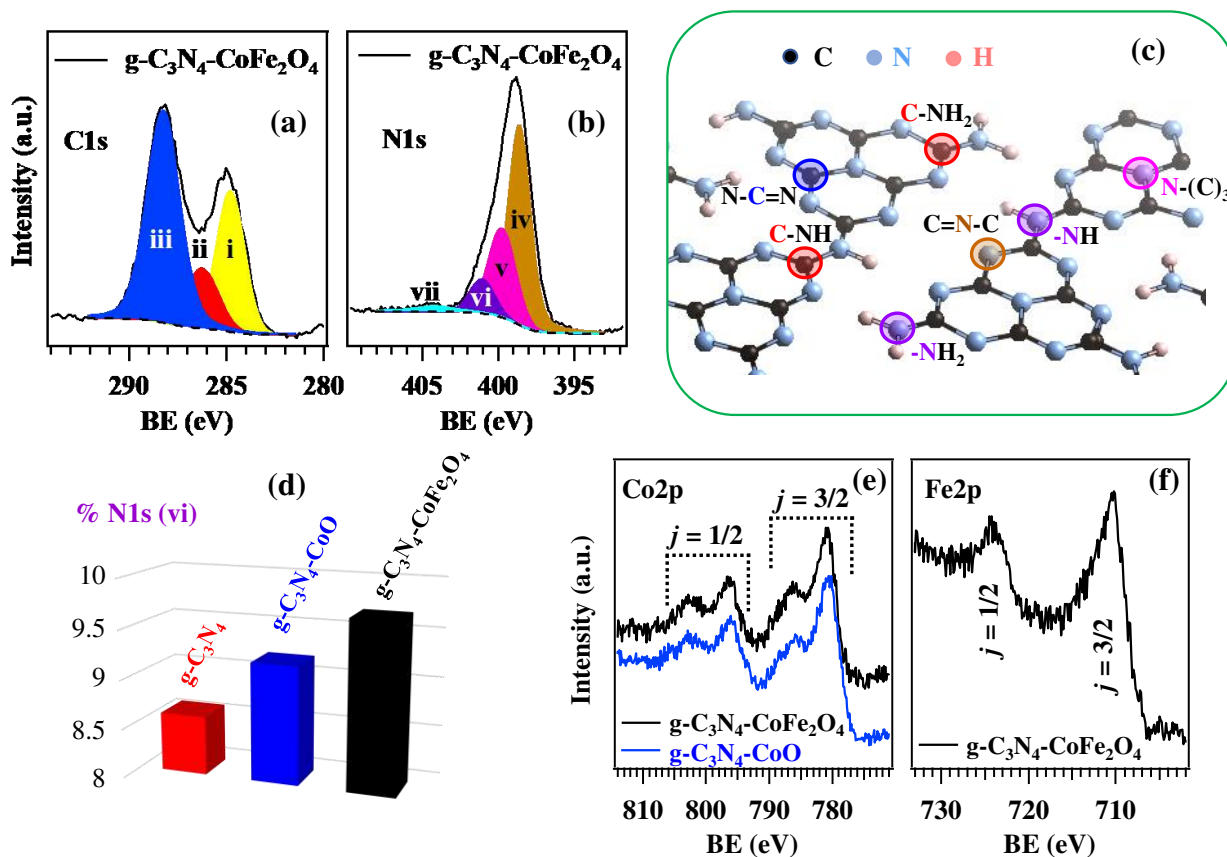


Fig. 2. Surface XPS analysis of carbon nitride-based specimens. (a) C1s and (b) N1s photopeaks for sample $g\text{-C}_3\text{N}_4\text{-CoFe}_2\text{O}_4$. (c) Schematic representation of graphitic carbon nitride structure [51], with the indication of non-equivalent carbon and nitrogen atoms. Color codes are the same as in panels (a) and (b). (d) Contribution of the (vi) N1s component to the overall N1s signal for the investigated specimens. Co2p (e) and Fe2p (f) photopeaks for $g\text{-C}_3\text{N}_4\text{-CoO}$ and $g\text{-C}_3\text{N}_4\text{-CoFe}_2\text{O}_4$ specimens.

due to π -electrons excitations in heptazine rings (mean BE = 404.2 eV) [16,39,47,52]. The contribution of component (vi) to the N1s signal (Fig. 2d and Table S3) increased according to the following sequence: $g\text{-C}_3\text{N}_4 < g\text{-C}_3\text{N}_4\text{-CoO} < g\text{-C}_3\text{N}_4\text{-CoFe}_2\text{O}_4$, suggesting a parallel enhancement of defects resulting from -NH_x presence, due, in turn, to carbon nitride bombardment during RF-sputtering. Such defects can act as capturing sites, minimizing charge carrier recombination and enhancing thus the system photoactivity [49,56]. Details on the O1s spectral features are reported in the SI (see Fig. S4, Table S4 and related comments).

The analysis of Co and Fe oxidation states in the target materials required particular attention. For both g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄ samples, the Co2p photopeak (Fig. 2e) had a qualitatively similar band shape and was characterized by intense shake-up satellites at BEs \approx 5.1 eV higher than the corresponding spin-orbit components. This indication was a clear fingerprint for the occurrence of high-spin Co(II) centers at the system surface [29-31,39,41,57]. For sample g-C₃N₄-CoO, the signal energy location [BE(Co2p_{3/2}) = 781.1 eV; spin-orbit splitting (SOS) separation = 15.7 eV] was in excellent agreement with the presence of CoO [16,18,34-35,39], with no other cobalt oxides in appreciable amounts. As a matter of fact, CoO occurrence can be deemed to be promising for the present applications, taking into account that nanocrystalline cobalt(II) oxide, differently from the corresponding bulk phase, possesses a very favorable activity as solar water splitting photocatalyst [29]. The lack of signals centered at 778.0-779.0 eV pointed out the absence of Co metal impurities [39].

As far as specimen g-C₃N₄-CoFe₂O₄ is concerned, the Co2p position underwent an upward shift of +0.2 eV with respect to g-C₃N₄-CoO. The obtained value [BE(Co2p_{3/2}) = 781.3 eV; see Fig. 2e] was compatible with that previously reported for Co centers in CoFe₂O₄-containing systems [33,55,58-59]. The Fe2p peak, free from evident shake-up satellites on the high BE sides of the main spin-orbit components [BE(Fe2p_{3/2}) = 710.6 eV; SOS = 13.3 eV], was in line with that reported for MFe₂O₄ with M = Mg, Co [17,31,33,53,57-58].

Material morphological organization was preliminarily investigated by FE-SEM analyses performed in different sample regions, that enabled to ascertain material lateral homogeneity. Bare g-C₃N₄ (Fig. S5) possessed a granular texture resulting from the assembly of uniformly interconnected grains with a broad dimensional distribution (500 nm - 4 μ m; mean deposit thickness = 13 μ m), yielding an open area deposit. Functionalized specimens displayed qualitatively similar features (Fig. 3), confirming thus that the adopted RF-sputtering conditions were mild enough to prevent appreciable modifications/alterations of the pristine g-C₃N₄.

Nonetheless, a detailed inspection of higher magnification FE-SEM images in Fig. 3 revealed the presence of globular nanoaggregates related to metal oxides deposited *via* RF-sputtering. In-plane elemental maps recorded by EDXS (Fig. S6 and S7) confirmed that, in line with XPS and TEM investigation (see below), CoO or CoFe₂O₄ were evenly dispersed on the underlying g-C₃N₄ deposit. In addition, cross-sectional line-scan analyses on functionalized samples (Fig. S8 and S9) pointed out that the presence of functionalizing metal oxides was not limited to the outer regions of carbon nitride deposits, but extended even to the inner ones. This behaviour indicated the occurrence of an intimate contact between g-C₃N₄ and the introduced complementary catalysts, an important issue to exploit their mutual interplay and obtain an enhanced functional activity (see below). Such a result was related to the synergistical combination of the inherent RF-sputtering infiltration power and the open area morphology of the used carbon nitride deposits [12,40].

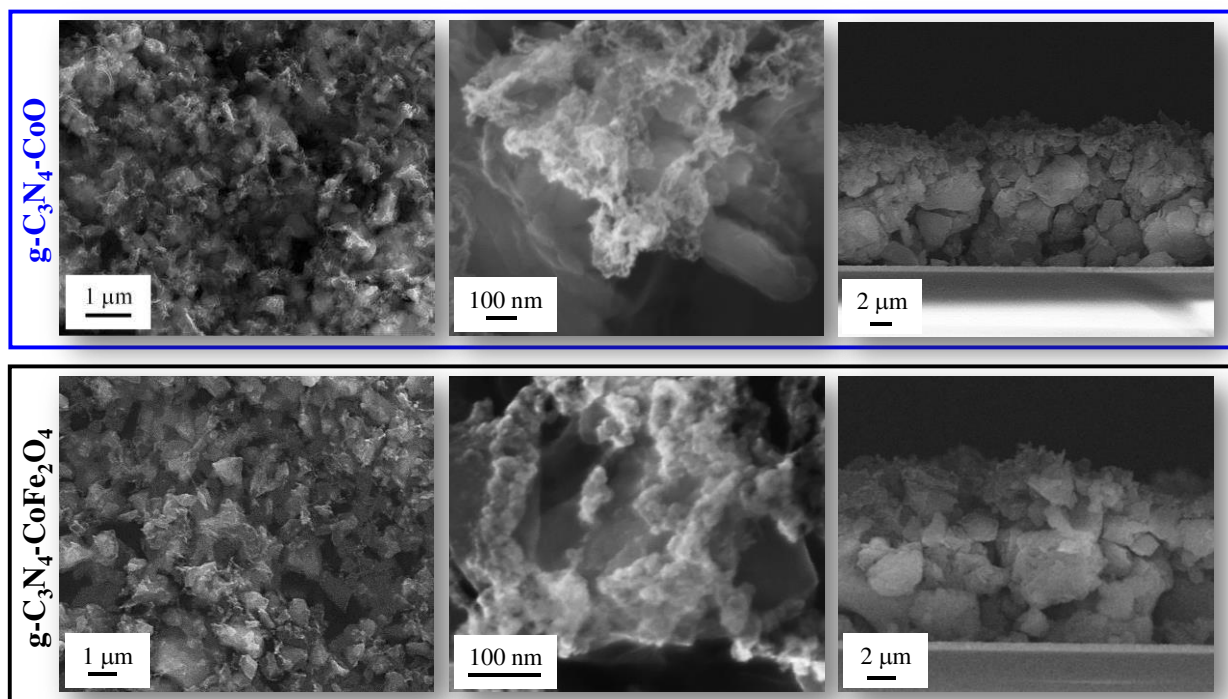


Fig. 3. Plane-view and cross-sectional FE-SEM images of g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄ electrodes.

Since X-ray diffraction (XRD) analyses (Fig. S10 and related observations) did not provide

any clear-cut evidence for the presence of CoO or CoFe₂O₄, carbon nitride peaks being the only detectable ones, efforts were devoted to an advanced investigation by TEM and related techniques, to better elucidate the system structure and nano-organization. SAED, as well as BF-STEM and HAADF-STEM were used for phase identification, whereas compositional analyses

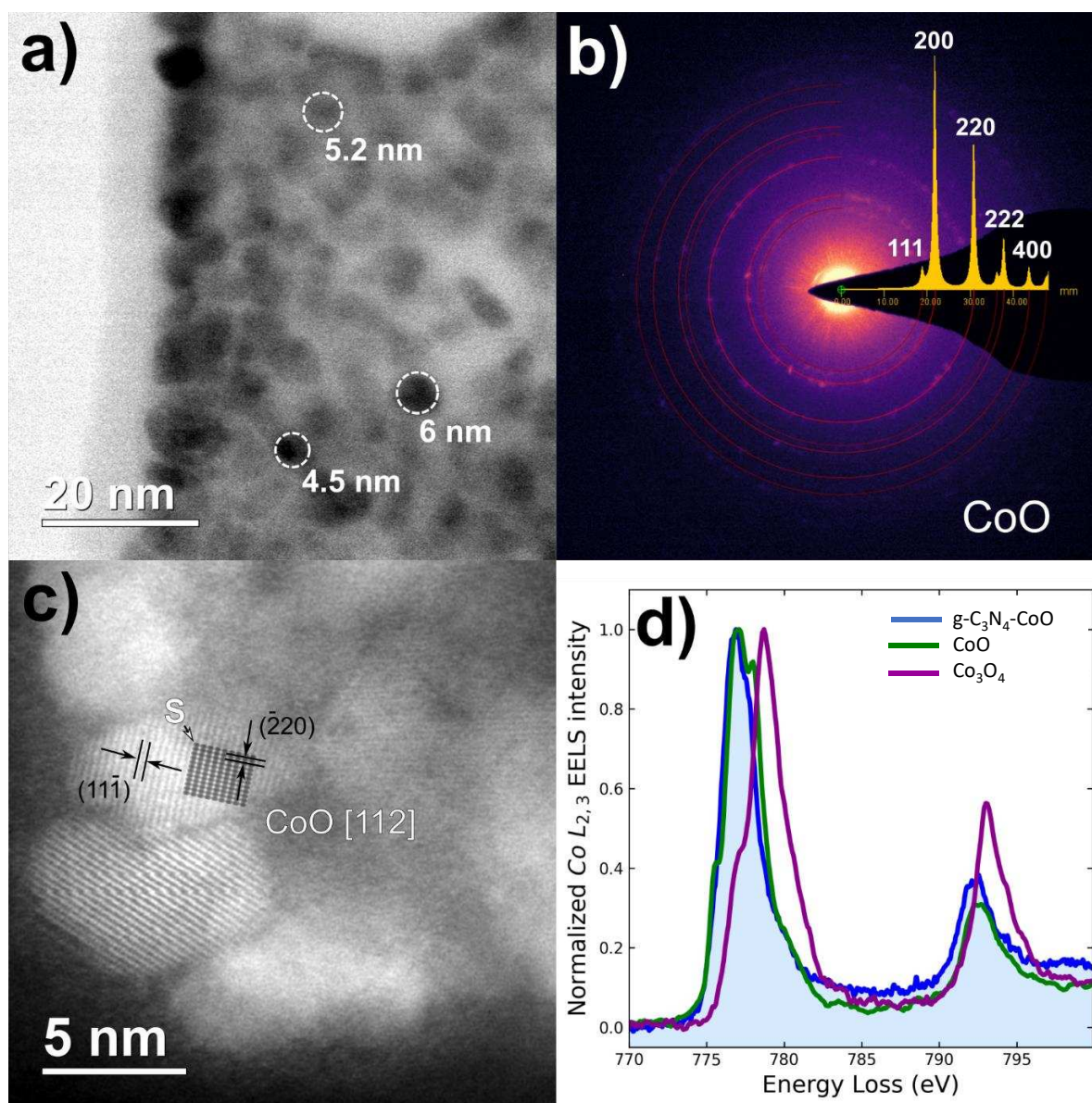


Fig. 4. TEM study of a g-C₃N₄-CoO specimen. a) BF-STEM image. b) Experimental and simulated (overlaid) SAED diffraction pattern showing the presence of the cubic CoO phase. c) Atomic resolution HAADF-STEM image of one CoO nanoparticle in the [112] zone axis, in good agreement with simulated image ('S'). d) EELS spectra of the Co *L*_{2,3} edge acquired on the nanoparticle (in blue) compared to reference spectra taken on CoO (green) and Co₃O₄ (purple) powders (see SI and Fig. S11).

were performed by EDXS and EELS.

For g-C₃N₄-CoO, spherical nanoparticles with average dimensions of (5±1) nm could be observed (Fig. 4a). The pertaining SAED pattern was characterized by rings featuring many diffraction spots, due to the contribution of various randomly oriented nanoparticles within the

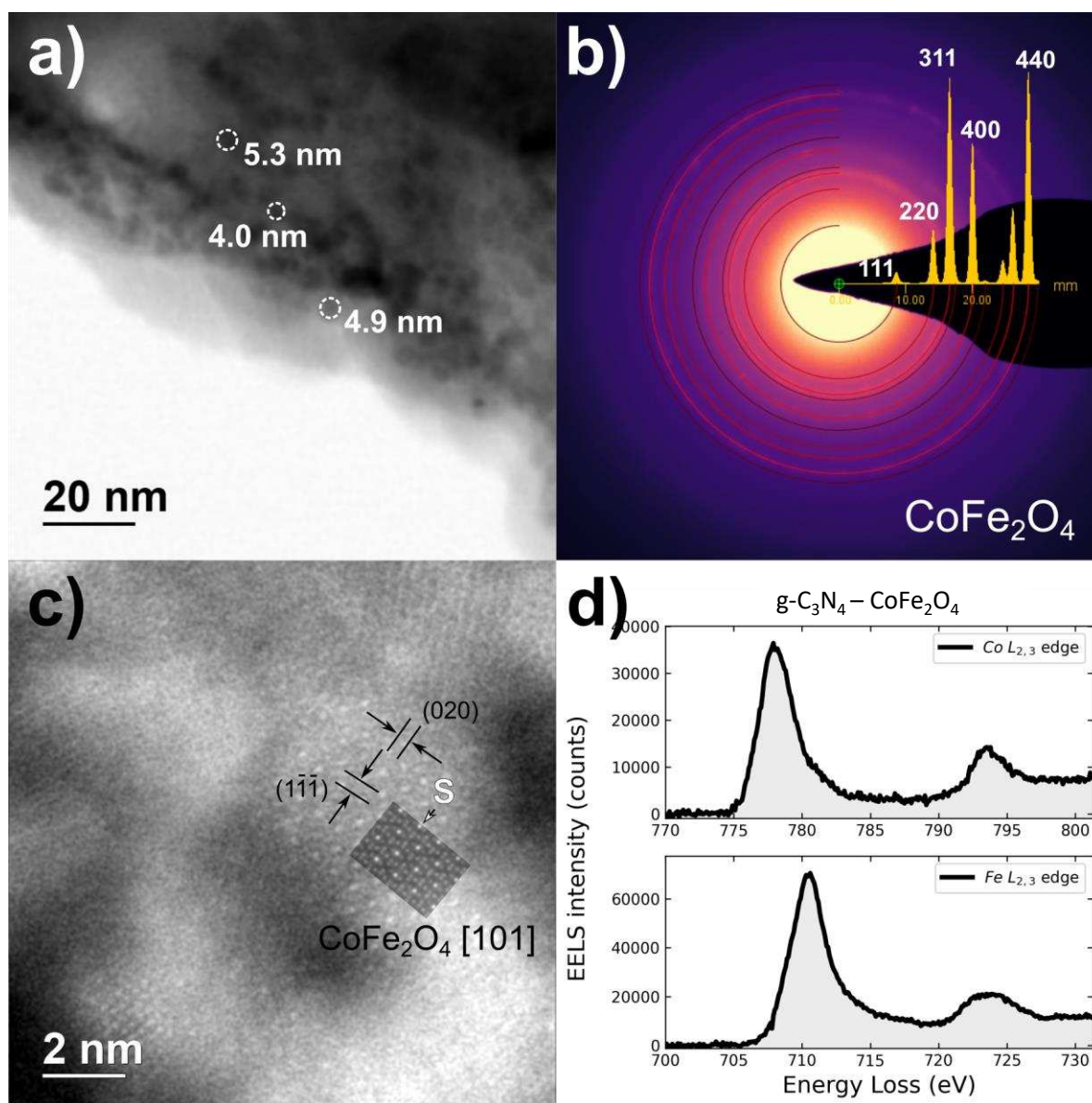


Fig. 5. TEM study of a g-C₃N₄-CoFe₂O₄ specimen. a) BF-STEM image. b) Experimental and simulated (overlaid) SAED diffraction pattern showing the occurrence of spinel-type CoFe₂O₄. c) Atomic resolution HAADF-STEM image of one CoFe₂O₄ nanoparticle in the [101] zone axis, in good agreement with simulated image ('S'). d) EELS spectra of the Co (top) and Fe (bottom) L_{2,3} edges acquired on the nanoparticle, in agreement with literature [60].

analyzed area. Comparison of d -spaces with data reported for the different cobalt oxides showed the best agreement with cubic CoO [61], which was confirmed to be phase pure by overlaying a simulated diffraction pattern (Fig. 4b). These results were in excellent agreement with XPS ones (see above and Fig. 2). High resolution (HR) HAADF-STEM imaging showed a CoO nanoparticle in [112] zone axis, in good accordance with the simulation (Fig. 4c, indicated by ‘S’). EELS analysis of the Co $L_{2,3}$ edge recorded on the nanoparticles (blue spectrum in Fig. 4d) presented a high similarity with that of a CoO reference [62-63], in line with the results obtained by the analysis of the O K edge (Fig. S12).

Analysis of g - C_3N_4 - $CoFe_2O_4$ specimen shows crystalline nanoparticles with a mean diameter of (5 ± 1) nm (Fig. 5a). A comparison of the experimental SAED pattern with available ones for known Co-Fe-O phases showed the best agreement with spinel-type $CoFe_2O_4$ [64] (Fig. 5b). The presence of the latter, revealed also by XPS data, was further supported by the good agreement between simulated and experimental HAADF-STEM images shown in Fig. 5c, as well as by a careful comparison with literature data [60,65] of EELS spectra of Co $L_{2,3}$, Fe $L_{2,3}$ (Fig. 5d) and O K (Fig. S13) edges.

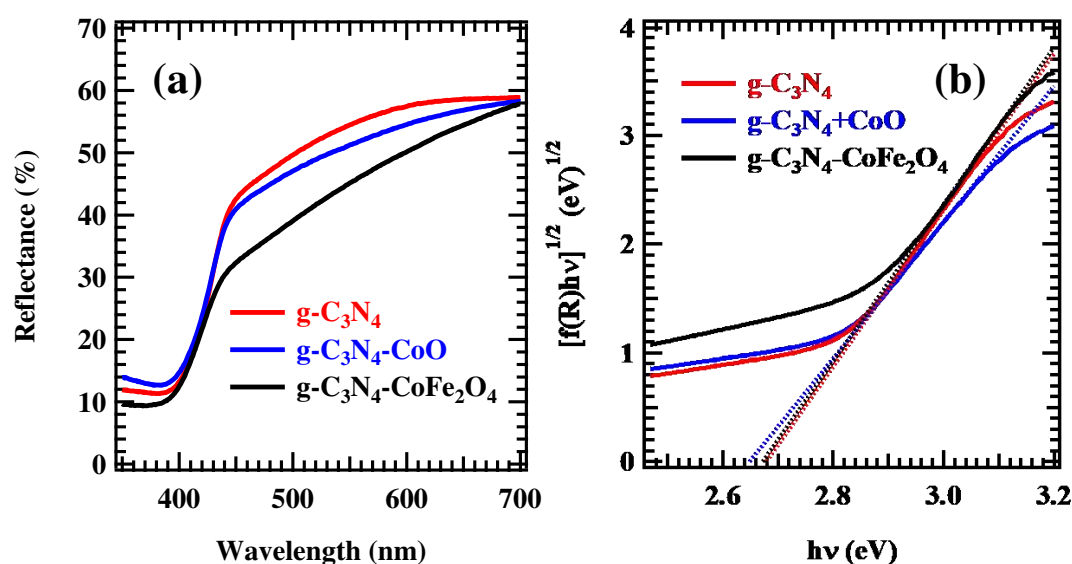


Fig. 6. (a) Diffuse reflectance spectra and (b) Tauc plots for bare and functionalized carbon nitride samples supported on FTO.

In order to evaluate the light-harvesting properties of the prepared samples as OER photoanodes, optical absorption analyses were carried out. The recorded spectra (Fig. 6a) were dominated by a net reflectance decrease at $\lambda < 450$ nm, corresponding to interband electronic transitions in carbon nitride [66-68], the predominant system component (see XPS results). In line with this observation, the optical band gap (E_G), obtained from Tauc plots in Fig. 6b, was very similar for all samples (average value = 2.67 eV) [12,16,30,34,39,69]. These outcomes also indicated that no carbon nitride doping, with consequent creation of impurity levels in the band gap, took place under the adopted processing conditions. Nevertheless, a detailed inspection of the recorded optical spectra showed a reflectance decrease (*i.e.*, an absorption increase) in the Vis spectral region upon functionalization of bare g-C₃N₄ samples, especially in the case of g-C₃N₄-CoFe₂O₄. This phenomenon, in accordance with previous studies [17,26,34,69], is one of the issues accounting for the improved photoactivity of functionalized carbon nitride materials (see below).

3.2 Photoelectrochemical tests

The results of OER functional tests performed on the target systems are presented in Fig. 7 (see also Tables S5-S6 and Fig. S14). Chopped light LSV analyses (Fig. 7a) showed good current density values already below the water oxidation thermodynamic potential. The current density values, provided in Table S5-S6, are in line with those reported by other authors for homologous systems (see Table S7). In particular, a comparison of LSV scans reveals a favourable photocurrent density increase upon g-C₃N₄ functionalization with the target complementary catalysts, according to the following sequence: g-C₃N₄ < g-C₃N₄-CoO < g-C₃N₄-CoFe₂O₄ (Fig. 7b). This photoactivity order was in perfect agreement with the information gained by ABPE curves (Fig. 7c), showing a favourable shift of the whole profile to lower potential values in comparison to bare g-C₃N₄ and confirming that g-C₃N₄-CoFe₂O₄ was the best performing

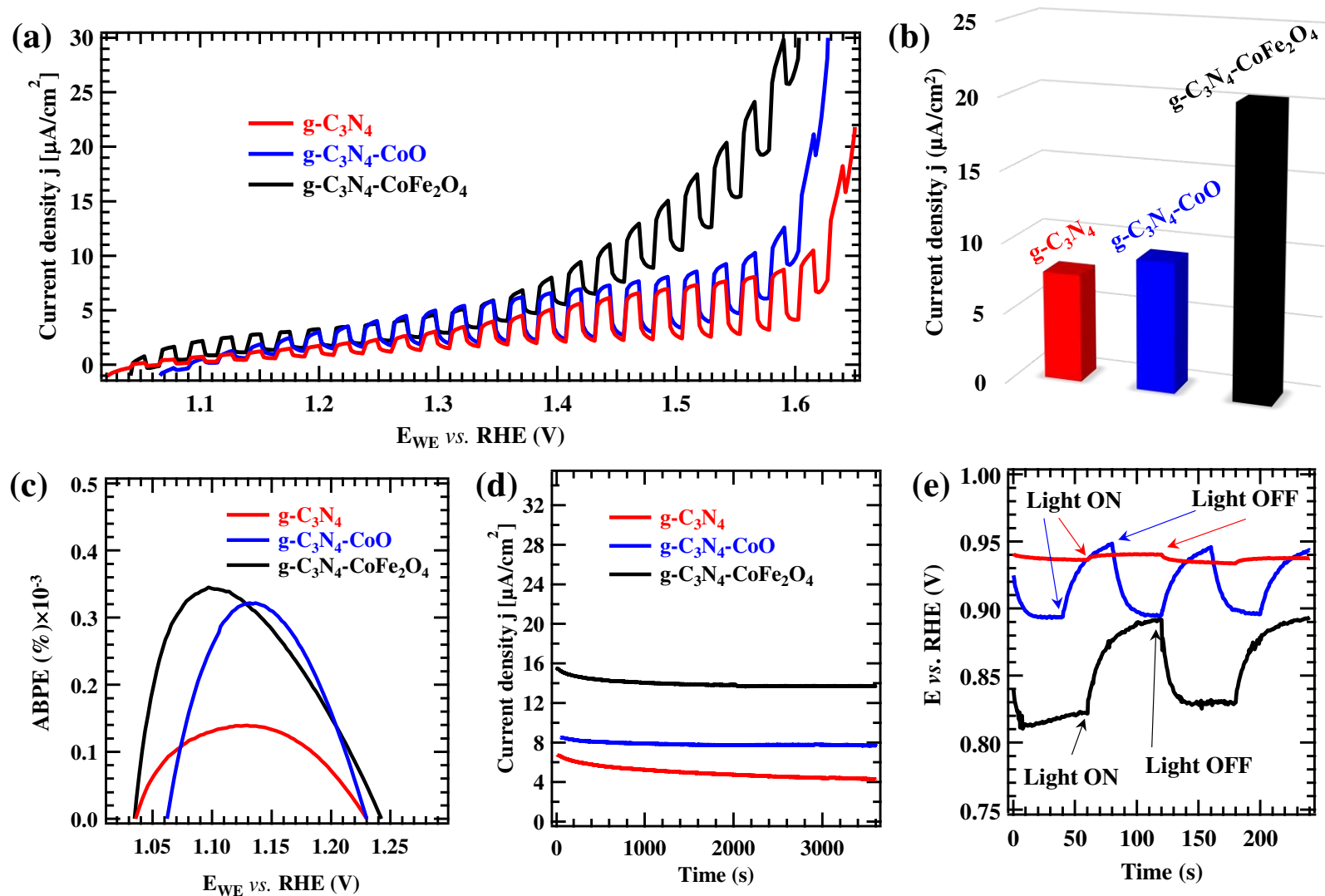


Fig. 7. Photoelectrochemical characterization of bare and functionalized carbon nitride electrodes. (a) Chopped light linear sweep voltammeteries. Corresponding photocurrent density values at 1.5 V vs. RHE (b), ABPE % curves (c), CA curves registered at 1.5 V vs. RHE (d), and photopotential curves collected at the open circuit potential (OCP) with LED light pulses of 50 mW/cm^2 (e).

photoanode (see the data in Table S5). Tafel plots acquired in the dark and under illumination (Fig. S14) yielded slope values favourably comparing with analogous catalysts previously reported in the literature, as well as with various benchmark electrode materials based on IrO_2 and RuO_2 (compare the data in Table S6 with the ones in Tables S7-S8).

In view of practical applications of the developed systems as OER electrocatalysts, the assessment of material service life is an important issue. In the case of g- C_3N_4 -based systems, the stability is known to be directly affected by both the adopted preparation route and the system engineering by combination with other suitable agents [21]. In this work, a preliminar investigation in this regard was accomplished by CA measurements for a total duration of 1 h. The obtained results (Fig. 7d) revealed that for the pristine g- C_3N_4 a current density loss of 36.4% took place, whereas the presence of functionalizing agents yielded an improved material durability, reducing the observed photocurrent decrease to 9.1% and 11.3 % for g- C_3N_4 -CoO and g- C_3N_4 - CoFe_2O_4 , respectively. These latter variations were lower than those reported for g- C_3N_4 -based systems as such [48], incorporated with Co^{2+} [30] or combined with Au and/or Ag [12,70], TiO_2 [46], MnCo_2O_4 [71], Co_3O_4 [25], SnO_2 and SnS_2 [72], $\text{Co}(\text{OH})_2$ [26], $\text{Ni}(\text{OH})_2$ [73], CuTi- and NiFe-layered double hydroxides [45,74], as well as on mixed Co nitride and oxide nanofragments encapsulated in nitrogen-doped carbon nanostructures [75]. In addition, the target materials were stored for six months under ordinary laboratory conditions and tested every 90 days as OER photoanodes. The results revealed the occurrence of very modest photocurrent density variations (Fig. S15), confirming a good operational stability. This conclusion was further validated by XPS analyses performed after long-time operation (see Fig. S16; compare with Fig. 2a,b,e,f and with Fig. S2, S3 and S4) and XRD (Fig. S17; compare with Fig. S10), that allowed to rule out appreciable degradation/dissolution phenomena upon prolonged photoelectrochemical testing. Taken together, these issues underline the applicative potential of the present systems, free from toxic and expensive noble metals and endowed with a very low content of functionalizing agents, towards the development of cost-effective OER electrocatalysts for real-world applications.

The attractive performance improvement resulting by g-C₃N₄ functionalization with low amounts of CoO and CoFe₂O₄ can be attributed to the synergistic concurrence of different factors. Beside the enhanced radiation absorption and the increased nitrogen defect content, promoting charge carrier separation (see the above UV-Vis and XPS data), a main contributing effect is due to the close contact between g-C₃N₄ and the introduced functionalizing agents, resulting, in turn, in the efficient formation of junctions boosting electron-hole separation.

A detailed examination of the latter junctions can indeed enable a deeper insight into the underlying mechanism. When a semiconductor is in contact with a solution, the thermal equilibrium established at the interface causes a band bending due to Fermi level (E_F) shifting, and the occurrence of a voltage drop across the space charge layer. The E_F energy position can be determined by measuring the open circuit potential (OCP) with respect to the reference electrode [76]. This calculation was performed for all the investigated materials, obtaining a value of ≈ 1.0 V vs. RHE, which was used as a starting point to build up the schematic diagrams reported in Fig. 8. The difference between E_F and the valence band (VB) edge energies enabled us to set the VB edge position for g-C₃N₄ ($VB - E_F \approx 1.65$ eV [77]), CoO ($VB - E_F \approx 0.31$ eV [78]), and CoFe₂O₄ ($VB - E_F \approx 1.22$ eV [77]) on the RHE scale. Basing on the band gap values of g-C₃N₄ (2.67 eV, determined by optical measurements; see above), CoO (2.50 eV [79]), and CoFe₂O₄ (1.70 eV) [77]), the corresponding conduction band (CB) edge positions can be subsequently derived. It is worthwhile noticing that, for both g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄, experimental results are compatible only with an *n*-type behaviour of the overall electrocatalyst (see also below), in agreement with the fact that graphitic carbon nitride is the predominant system component. This implies that, in the case of g-C₃N₄-CoO, the formation of a *p-n* junction must be considered, since electrons must reach the counterelectrode through g-C₃N₄ flakes, the material in contact with the FTO substrate. In fact, a *Z*-type scheme, leaving electrons in the CoO conduction band, would not account for the system activity.

In a different way, in the case of g-C₃N₄-CoFe₂O₄, a *Z*-scheme junction is the only possibility

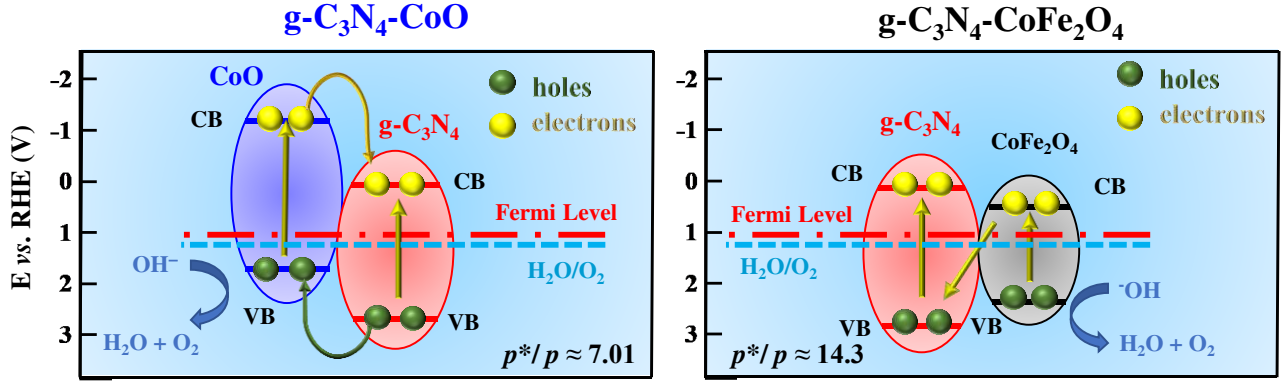


Fig. 8. Approximate representation of the junction between g-C₃N₄ and CoO (left) or CoFe₂O₄ (right) [12,77,79]. Despite CoO is known to undergo a progressive transformation into Co₃O₄ upon prolonged air exposure, in the present case, all the performed analytical characterizations revealed the occurrence of phase-pure CoO. As a consequence, Co₃O₄ was not taken into account in the construction of the energy band diagram proposed in Fig. 8.

enabling to explain the observed behaviour. The experimental proof for the existence of this Z-scheme junction is provided by the increase in the photocurrent density and ABPE values observed upon carbon nitride functionalization (see Fig. 7a-c), and further useful indications are provided by measuring the OCP shift upon illumination. A negative shift in the OCP position indicates an *n*-type behaviour of the investigated material, and a corresponding upward band bending [80]. This behaviour was confirmed for all the investigated specimens, but with important differences. It is worthwhile recalling that the amplitude of the OCP position shift upon illumination corresponds to a photopotential (ΔE_{ph}) which, for an *n*-type semiconductor with a relatively higher impurity concentration ($\geq 10^{17} \text{ cm}^{-3}$), can be expressed as [80-81]:

$$\Delta E_{\text{ph}} = (K_{\text{B}}T/e) \times \ln(p^*/p) \quad (3)$$

where K_{B} is the Boltzmann constant, T is the absolute temperature (in K), p^* is concentration of holes generated under illumination, whereas p is the corresponding value in the dark. The photopotential curves recorded as a function of time upon intermittent illumination (Fig. 7e) are respectively ≈ 5 , 50 and 70 mV for pristine g-C₃N₄, g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄, respectively. These values enable to calculate, using equation (3) at room temperature, the following p^*/p ratios: 1.21, for g-C₃N₄; 7.01,

for g-C₃N₄-CoO; 14.3, for g-C₃N₄-CoFe₂O₄. The large increase in p^*/p values for g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄ in comparison to bare carbon nitride can be explained by a more efficient separation of photogenerated charge carriers, thanks to the formation of p - n or, even better, Z -scheme junctions between g-C₃N₄ and the introduced complementary catalysts. The occurrence of these junctions finds its counterpart in higher photocurrent densities in the reported chopped LSVs (see Fig. 7a-b).

4. Conclusions

This study has focused on the functionalization of supported carbon nitride materials with a minimum amount of complementary catalysts capable of boosting the resulting photoelectrochemical activity in the oxygen evolution reaction. Specifically, g-C₃N₄ deposits have been fabricated on FTO substrates by a simple decantation from isopropanol suspensions, followed by functionalization with very low amounts of CoO or CoFe₂O₄ nanoparticles by RF-sputtering, and final thermal treatment in an inert atmosphere. The outcomes of a multi-technique investigation revealed, for g-C₃N₄-CoO and g-C₃N₄-CoFe₂O₄, the formation of pure materials featuring an intimate contact between the system components, a higher Vis light absorption and an enhanced defect content in comparison to the pristine carbon nitride. Taken together, these features were responsible for an enhanced activity in photoassisted OER processes, especially for g-C₃N₄-CoFe₂O₄. The obtained results were rationalized basing on the formation of carbon nitride/oxide heterojunctions, whose nature was directly dependent on the used complementary catalyst, affording an enhanced separation of photogenerated electrons and holes. These characteristics were accompanied by a favorable time stability even in comparison to various previously reported g-C₃N₄-based materials, a feature of remarkable interest for eventual practical end-uses.

Overall, our work demonstrates a simple and potentially scalable methodology for the preparation of carbon nitride photoanodes with improved photoelectrochemical performances by the introduction of functionalizing agents in a very low amount. Indeed, the proposed strategy opens new

opportunities for the development of efficient electrocatalysts for clean energy production. Yet, additional efforts will have to be devoted to further refinements of material long-term stability under various operational conditions, and to properly address issues limiting the photon-to-current efficiency, in order to progress towards performances enabling commercial viability. Future work will be also dedicated to the design and development of g-C₃N₄-oxide materials on porous metallic scaffolds, endowed with a large active area and a desirable electrical conductivity, not only as OER photoanodes, but even as electrocatalysts for water purification. The implementation of active functional systems simultaneously enabling energy production and water purification possesses in fact a strategical importance for a future sustainable development.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.XXX>.

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