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2 Hybrid photoelectrocatalytic TiO₂-Co₃O₄/Co(OH)₂ materials 3 prepared from bio-based surfactants for water splitting

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15 **Abstract:** The development of new photoanode materials for hydrogen production and water
16 treatment is in full progress. In this context, hybrid TiO₂-Co₃O₄/Co(OH)₂ photoanodes prepared by
17 the sol-gel method using biosurfactants are currently being developed in our group. The combina-
18 tion of the TiO₂ with cobalt-based compound significantly enhances the visible absorption and
19 electrochemical performance of the thin films, which is mainly due to an increase in the specific
20 surface area and a decrease in the charge transfer resistance at the surface of the thin films. The
21 formation of these composites allows a 30-fold increase in the current density when compared to
22 cobalt-free materials, with the best TiO₂-Co_{0.5} sample achieving a current of 1.570 mA.cm⁻² and a
23 theoretical H₂ production rate of 0.3 μmol.min⁻¹.cm⁻² under xenon illumination.

24 **Keywords:** composite materials, photoanodes, water splitting, heterojunctions, titanium oxides,
25 cobalt oxides

27 1. Introduction

28 One of the most attractive solutions for reducing air pollution and slowing down
29 global warming is the use of "green" hydrogen as an energy carrier. By using a
30 photoelectrochemical cell (PEC) at the interface between water electrolysis and
31 photocatalysis, hydrogen can be produced without greenhouse gas emissions [1–3].
32 Moreover, the use of partially polluted water as a resource for this cell would allow the
33 coupling of green hydrogen production with tertiary water treatment [4–8]. In this re-
34 spect, work on the components of this cell, especially the photoanodes, is essential to
35 make such a system competitive.

36 The photoanode plays a key role in a PEC. It receives the light and generates the
37 charges necessary for the oxidation reaction of the water on its surface and, consequently,
38 for the production of hydrogen at the counter electrode, as well as for the mineralization
39 of the organic pollutants present in the water (in the case of polluted water as a resource).
40 This must be of the semiconductor type, and our choice fell on TiO₂, already known for
41 its photocatalytic properties, among other advantages [9–11]. However, TiO₂ has disad-
42 vantages such as low absorption in the solar spectrum (limited to the UV range), rapid
43 charge recombination and low electronic conductivity [12–14]. The formation of a
44 heterojunction combining the n-type TiO₂ semiconductor with a p-type semiconductor

45 can improve these properties [15–18]. Cobalt oxide has already proven itself as a dopant
46 for TiO₂ due to its high catalytic activity, low cost, stability in neutral and alkaline envi-
47 ronments and ability to be used as a bifunctional electrode [19,20]. Co₃O₄ has interesting
48 electronic properties which are an advantage for our application, and also a direct band
49 gap between 1.5 and 2.5 eV, which is essential for improving absorption in the visible
50 range [21–25]. Thus, this p-type semiconductor was chosen in this study to realize an
51 n-TiO₂ | p-Co₃O₄ type heterojunction.

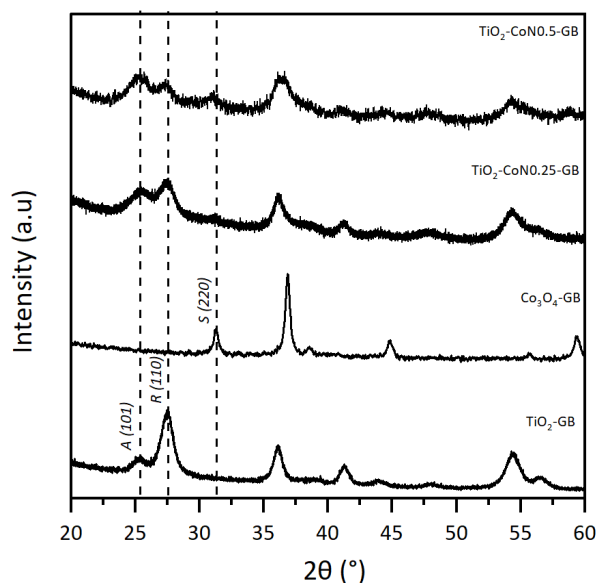
52 This kind of heterojunction has demonstrated enhanced electrochemical perfor-
53 mance through diverse synthesis routes such as hydrothermal route [26,27], anodization
54 [28], atomic layer deposition [29], metal organic chemical vapor deposition [30], im-
55 pregnation [31]. Regarding the sol-gel synthesis, it is rarely the only route used for n | p
56 materials, but it is often coupled with other synthesis routes. In this study, our goal was
57 to create photo-anodic materials using titanium and cobalt oxides along with different
58 bio-sourced surfactants via a new one-step sol-gel method. This synthesis method is
59 cost-effective, easy to implement, and could be transferred to other different types of
60 heterojunctions, allowing for a broader study. We have decided to use three different
61 surfactants and to introduce cobalt oxide in two molar ratios
62 (HNO₃/TTIP/Co(NO₃)₂•6 H₂O = 1/1/0.25 and 1/1/0.5) to allow a high degree of modularity
63 in terms of chemical composition, structural properties and, therefore, functional prop-
64 erties of the photoanodes in order to optimize their performances in water splitting.

65 2. Results and Discussion

66 2.1. Structural and textural characterization

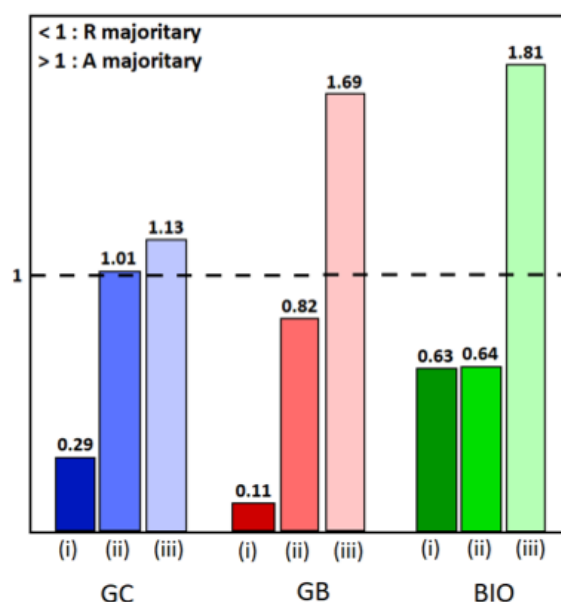
67 TiO₂/Co₃O₄ samples prepared with the GB surfactant were selected to illustrate the
68 XRD powder results in **Figure 1** with the diffractograms of TiO₂-GB, TiO₂-CoN0.25-GB,
69 TiO₂-CoN0.5-GB and Co₃O₄-GB. In order to compare the crystal structures of the
70 TiO₂-Co₃O₄ hybrid powders with those of the individual oxides, a Co₃O₄ powder (1:1:1
71 ratio) was synthesized using the same procedure as described above. On the TiO₂-GB
72 diffractogram, the presence of TiO₂ characteristic peaks was noted at 25.4° for the anatase
73 phase (A) and at 27.5° for the rutile phase (R) [32]. For the Co₃O₄-GB powder, a charac-
74 teristic peak of the spinel phase (S) was observed at 31.3° [33].

75 For XRD analysis, we used a copper (Cu) anticathode. The presence of cobalt (Co) in
76 our samples, an element close to Cu in the periodic table, leads to a fluorescence phe-
77 nomenon due to an absorption threshold close in energy to that of the incident beam. The
78 resulting diagram exhibits a high continuous background with high noise, which ob-
79 structs proper observation of the Co₃O₄ peaks in the composite materials diffractograms
80 (TiO₂-CoN0.25-GB and TiO₂-CoN0.5-GB). However, the three phases of the hybrid
81 powder are observable, and it is seen that the addition of Co₃O₄ does not affect the posi-
82 tion of the diffracted TiO₂ peaks, but does appear to affect the anatase/rutile phase ratio.



83
84 **Figure 1.** Powder diffraction patterns for TiO₂-GB, CO₃O₄-GB, TiO₂-CoN0.25-GB, and TiO₂-CoN0.5-GB.

85
86 To know more, the anatase and rutile proportions were calculated by Rietveld re-
87 finement and are reported in Table S1 [34]. As already displayed in our previous work,
88 the rutile phase predominates in the TiO₂ powders, but the anatase/rutile ratio varies
89 depending on the surfactant used [35]. For the hybrid powders, the influence of the ad-
90 dition of cobalt oxide on the TiO₂ phases is illustrated in the histogram (**Figure 2**). It can
91 be seen that the presence of the spinel phase causes a decrease in the proportion of the
92 rutile phase in favor of the anatase phase to the point where it becomes dominant. It ap-
93 pears that the presence of Co₃O₄ inhibits the effect of the surfactant on the formation and
94 stability of the anatase phase [36–38].



96
97 **Figure 2.** Histograms of anatase/rutile ratios (i) for TiO₂ type samples, (ii) for TiO₂-CoN0.25 type samples and, (iii) for
98 TiO₂-CoN0.5 type samples.

99
100 Calculation of the crystallite size was determined using Scherrer formula (1) with K
101 as the form factor (0.9 value for a spherical crystallite shape), λ as the CuK α wavelength

(in nanometers), HW as the half-width value (in radians), and θ as the corresponding diffraction angle (in radians). The results suggest cobalt oxide has a direct impact on the formation and size of anatase and rutile crystallites (refer to Table S2).

The crystallite size of the hybrid powders decreases independently of the type of surfactant, reaching values centered on 4 nm for the anatase phase and 6 nm for the rutile phase. The amount of cobalt oxide does not seem to have any influence, since the two ratios 0.25 and 0.5 induce similar crystallite size values. It can be concluded that the formation of the hybrid material containing the TiO₂/Co₃O₄ phase mixture allows a smoothing of the crystallite size of the different TiO₂ phases.

$$d = \frac{K \times \lambda}{HW \times \cos \theta} = \frac{0,9 \times 0,15406}{HW \times \cos \theta} \quad (1)$$

The BET isotherms for the hybrid materials show the same pattern, indicating the dual presence of microporosity and mesoporosity, as observed for TiO₂-GC in the previous work (Figure S1). Table 1 shows the specific surface areas, average sizes and pore distributions of the materials. The specific surface area of the materials formed by the two oxides is higher than that of the TiO₂ powders and increases with the amount of cobalt oxide. In fact, we find the following hierarchy TiO₂-CoN0.5 > TiO₂-CoN0.25 > TiO₂ in terms of specific surface area. This increase is particularly remarkable for GB and BIO samples, which reach specific surface areas of 97 and 126 m².g⁻¹ respectively for the highest Ti/Co ratio (0.5). For GC, whose specific surface area without cobalt was by far the highest, the increase is less, but the threshold of 126 m².g⁻¹ is reached for the same ratio (0.5). However, the average pore size of the hybrid materials does not change much between the different samples, making it difficult to correlate with the specific surface area. It seems that, as with the crystallite size above, the pore size for all TiO₂-Co₃O₄ materials homogenizes with the addition of cobalt to an average value of about 4.7 nm. The difference in specific surface area despite almost identical pore size could be explained by a difference in the size of the "mixed" aggregates.

Table 1. BET results.

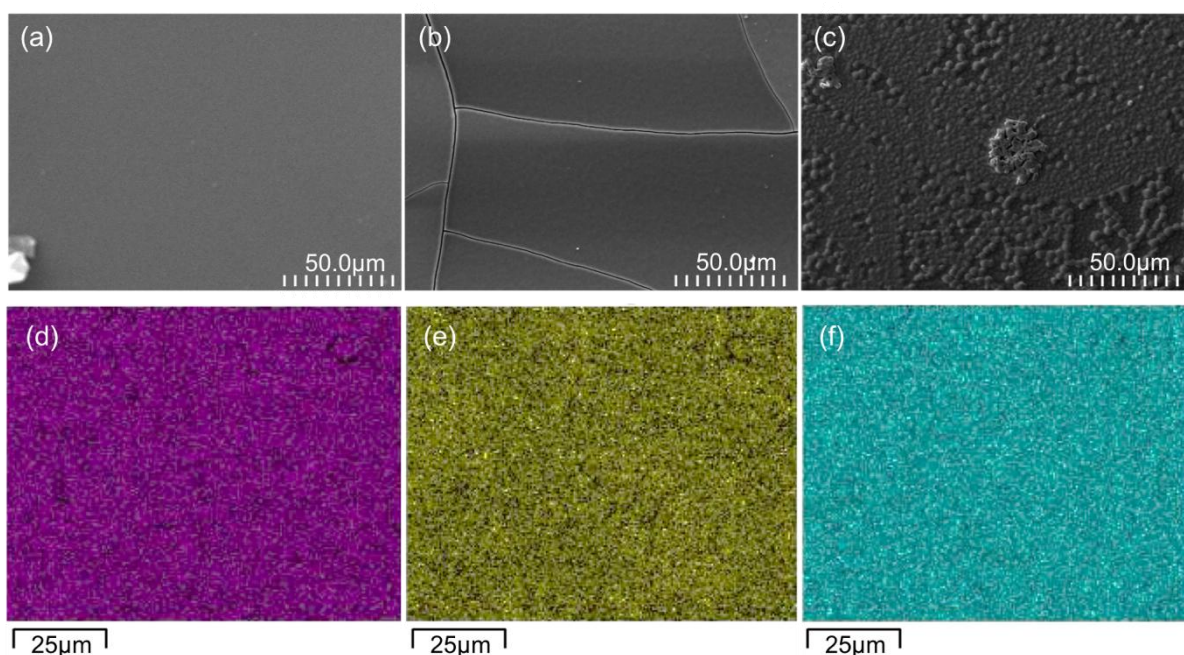
Samples	BET surface area (m ² /g)	Adsorption Average Pore Width (nm)	Pore size distribution (nm)
TiO ₂ -GC	101	2.66	Bimodal: 4 nm - 11 nm
TiO ₂ -CoN0.25-GC	112	4.85	Bimodal: 3.5 nm - 5 nm
TiO ₂ -CoN0.5-GC	126	4.27	Unimodal: 3.5 nm
TiO ₂ -GB	31	4.95	Bimodal: 4 nm - 60 nm
TiO ₂ -CoN0.25-GB	91	4.56	Bimodal: 3.5 nm - 5 nm
TiO ₂ -CoN0.5-GB	97	4.86	Unimodal: 3.5 nm
TiO ₂ -BIO	16	8.77	Bimodal: 3 nm - 9 nm
TiO ₂ -CoN0.25-BIO	88	5.82	Bimodal: 3.5 nm - 5 nm
TiO ₂ -CoN0.5-BIO	126	4.07	Unimodal: 3 nm

The pore size distribution for the TiO₂-CoN0.25 materials is similar, with all three samples showing a bimodal distribution centered at around 3.5 nm and 5 nm. A monodispersity is observed for the 3.5 nm pore size and a polydispersity for the 5 nm pore size (Figure S2). The same observation can be made for the TiO₂-CoN0.5 type materials, which have the highest cobalt loading, with the three samples showing the same type of distribution. For the 0.5 ratio, it can be observed a unimodal and monodispersed distribution centered at around 3.5 nm for GC and GB and closer to 3 nm for BIO (Figure S3). Through the pore size distribution, we again find a homogenization effect of the properties of the samples due to the addition of cobalt oxide. Based on the above results, only the samples synthesized with the GC surfactant with the highest specific surface

143 area ($\text{TiO}_2\text{-GC}$, $\text{TiO}_2\text{-CoN0.25-GC}$ and $\text{TiO}_2\text{-CoN0.5-GC}$) will be further characterized in
144 the following.
145

146 2.2. Morphological and chemical characterization

147
148 SEM images of the surface of the three GC-based thin films deposited on ITO sup-
149 port are shown in **Figure 3**. The surface of the $\text{TiO}_2\text{-GC}$ thin film (**Figure 3.a**) is smooth
150 and free of imperfections, which is not the case with the addition of Co_3O_4 . At a ratio of
151 0.25 (**Figure 3.b**), cracks appear, probably due to the change in surface tension caused by
152 the addition of Co, but the surface of the thin film remains smooth.
153



154
155 **Figure 3.** SEM images of the surface (a) $\text{TiO}_2\text{-GC}$, (b) $\text{TiO}_2\text{-CoN0.25-GC}$ (c) $\text{TiO}_2\text{-CoN0.5-GC}$ and EDX mapping of
156 $\text{TiO}_2\text{-CoN0.5-GC}$ sample, in pink (d) distribution of Ti element, in yellow (e) Co element, in blue (f) O element.

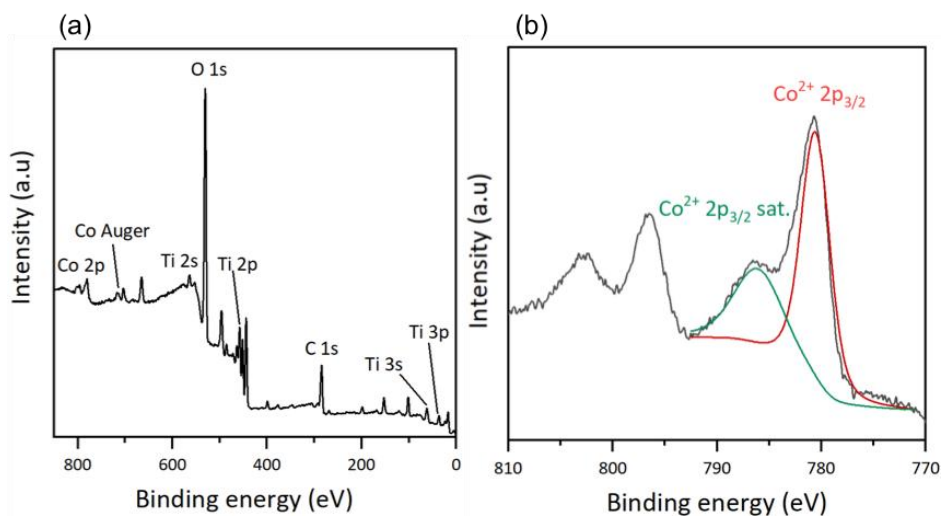
157
158 On the other hand, when the ratio is increased to 0.5 (**Figure 3.c**), the appearance of
159 the thin film surface is completely changed. A surface consisting of aggregates of TiO_2
160 and Co_3O_4 nanoparticles is observed. This was confirmed by a $5\ \mu\text{m} \times 5\ \mu\text{m}$ surface to-
161 pography measurement by AFM (not shown) which demonstrated an increase in the
162 arithmetic surface roughness from 0.8 nm for TiO_2 to 3.8 nm and 11.5 nm for Co_3O_4 ratios
163 of 0.25 and 0.5, respectively. The thicknesses of the thin films are approximately the same
164 with a total value of 1100 ± 350 nm.

165 The EDX analysis indicates that the Ti, Co, and O elements are uniformly distributed
166 throughout the $\text{TiO}_2\text{-CoN0.5-GC}$ thin film (**Figure 3.d, e, and f**). This observation is also
167 true for the other $\text{TiO}_2\text{-CoN0.25-GC}$ thin film, whose EDX profiles are not shown here.
168 Via a semi-quantitative study of EDX maps, the elemental composition ratios Co/Ti for
169 the $\text{TiO}_2\text{-CoN0.25-GC}$ and $\text{TiO}_2\text{-CoN0.5-GC}$ samples are determined to be 0.27 and 0.59,
170 respectively.

171 XPS analysis was performed to determine the surface composition of the thin films.
172 For the hybrid materials, the total spectrum of the $\text{TiO}_2\text{-CoN0.5-GC}$ sample is shown in
173 **Figure 4.a** and is similar to those of the other samples regardless of the ratio used. In the
174 total spectrum, we observe the presence of the same chemical elements as in the TiO_2 thin

175
176
177

films (C, O, Ti and Sn, In from the ITO substrate) and, in addition, the cobalt Co 2p appears at high binding energies [35]. The Co Auger peak corresponds to the emission of an electron during the de-excitation of the Co atom.



178

179 **Figure 4.** XPS results (a) survey of TiO₂-CoN0.5-GC, (b) Co2p scan after deconvolution of TiO₂-CoN0.5-GC.

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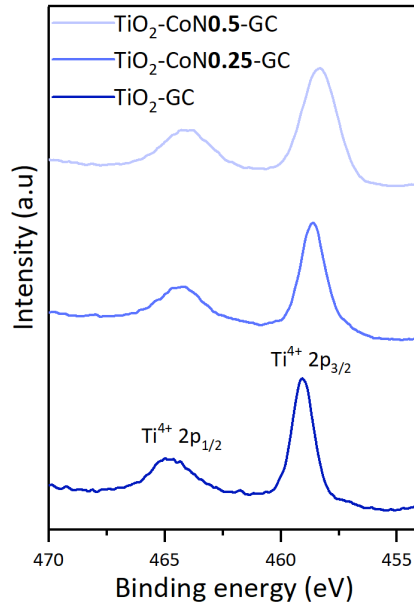
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To verify the nature of the cobalt on the surface of the thin films, a high-resolution deconvolution of the Co 2p spectrum was performed (**Figure 4.b**). A main peak related to Co²⁺ 2p_{3/2} at 780.5 eV and its satellite peak at 786.0 eV can be identified. The presence of a satellite peak is characteristic of the Co²⁺, outgoing electron interacting with a valence electron and exciting it, thereby shaking it to a higher energy level. As a consequence, the energy of the core electron is reduced and a satellite structure appears a few eV below the core level position, it's a shake-up type peak satellite [39,40]. Cobalt oxide Co₃O₄ is a mixed valence compound, cobalt exists in two oxidation states: Co²⁺ and Co³⁺. However, the deconvolution shows only the presence of Co²⁺, suggesting that cobalt in its oxidation state (III) does not exist on the surface of mixed thin films. According to Biesinger, M. C. et al, the position and shape of the Co²⁺ 2p_{3/2} peak indicates the presence of cobalt in the form of Co(OH)₂[41]. Since XPS gives access to a surface measurement, the cobalt oxide has probably adsorbed water molecules, inducing the formation of Co-O bonds, the oxygen coming from the water molecules. This hydroxide form on the surface of the materials applies to both mixed materials regardless of the Co ratio.

To evaluate the effect of the addition of cobalt oxide on the titanium oxide, the Ti 2p spectra for the three samples synthesized from the GC surfactant are shown in **Figure 5**.

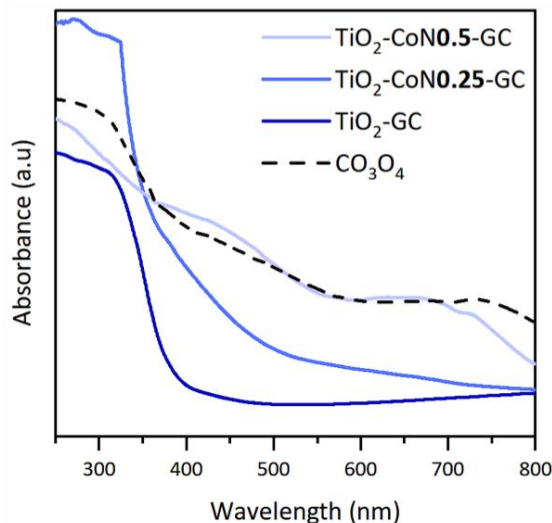


199
200 **Figure 5.** Comparison of Ti 2p scan of the three thin films.

201
202 The Ti 2p spectra display two symmetrical peaks corresponding to Ti 2p_{1/2} and Ti
203 2p_{3/2}, representing Ti⁴⁺ in TiO₂. With the incorporation of Co, there is a subsequent shift to
204 lower binding energies (+0.5 eV for TiO₂-CoN0.25 and 0.2 eV for TiO₂-CoN0.5), indicating
205 the occurrence of electron transfer between Co₃O₄/Co(OH)₂ and TiO₂. This transfer es-
206 tablishes an interaction between them, which can facilitate surface charge separation and
207 enhance the photocatalytic activity of the thin films [42,43].

208 2.3. Optical Properties

209
210 In order to determine the evolution of the absorption of the thin films in the visible
211 region, UV-visible-NIR spectra were studied. TiO₂ is an oxide that absorbs mainly in the
212 UV region (from 100 to 400 nm), while Co₃O₄ absorbs in the visible region (from 400 to
213 780 nm). **Figure 6** shows the absorption spectra of the samples. The TiO₂ thin film spec-
214 trum is characteristic of TiO₂ with absorption at wavelengths below 400 nm. With the
215 addition of a small amount of cobalt oxide, a shift of the absorption towards the visible
216 region is observed as well as an increase in absorbance compared to the cobalt-free sam-
217 ple.



219 **Figure 6.** UV-visible spectroscopy data with an absorption spectra of GC samples and Co₃O₄.

220 The absorption spectrum of the TiO₂-CoN0.5 thin film shows that increasing the Co
221 content reinforces the above observations. Therefore, it can be concluded from the ab-
222 sorption spectra that the addition of cobalt oxide has the desired effect of increasing the
223 absorption in the visible region for the TiO₂-CoN0.25 and TiO₂-CoN0.5 samples. Figure 6
224 shows that the absorption profile of the cobalt oxide is similar to that previously high-
225 lighted for the TiO₂-CoN0.5 thin films, indicating that the cobalt oxide is at the origin of
226 the improvement in the optical properties of the mixed materials. To determine the band
227 gap of the thin films, the Tauc diagram was constructed by plotting the coefficient
228 $(\alpha h\nu)^n$ as a function of energy E in eV. The value of the band gap was obtained by ex-
229 trapolating the linear portion of the curve at the intersection of this line with the x-axis.

230 The absorption coefficient α (cm⁻¹) and the frequency ν (Hz) can be determined
231 from equations (2) and (3), where A is the absorbance, e is the thickness of the thin film
232 (cm), c is the speed of light (m.s⁻¹), and λ is the wavelength (m).
233

$$234 \quad \alpha = \frac{A}{100} \times \frac{1}{e} \quad (2)$$

$$235 \quad \nu = \frac{c}{\lambda} \quad (3)$$

236
237
238 The coefficient n is related to the type of band gap, namely $n = 0.5$ for an indirect
239 band gap (anatase phase) or $n=2$ for a direct band gap (rutile and spinel phases).

240 The energy E (eV), can be determined using equation (4), where q is the elemen-
241 tary charge ($1.6 \cdot 10^{-19}$ C) et and h is Planck's constant ($6.63 \cdot 10^{-34}$ J.s):
242

$$243 \quad E = \frac{h\nu}{q} = \frac{hc}{\lambda q} \quad (4)$$

244
245 The theoretical value of the indirect band gap of the anatase phase is 3.2 eV and that
246 of the direct band gap of the rutile phase is 3.0 eV. For the spinel phase of cobalt oxide,
247 the direct band gap is between 1.5 and 2.5 eV. It is interesting to compare these theoretical
248 values with the experimental values determined by the Tauc plot and presented in Table
249 2, distinguishing between the indirect and direct band gaps. For the TiO₂ thin film, an
250 indirect band gap lowers that of the anatase phase is obtained, with a value of 2.87 eV.
251 This difference between the experimental and theoretical values is not surprising, con-
252 sidering the minority of the anatase crystal phase in the compound (22%). For the direct
253 band gaps, the experimental value is 3.37 eV, which is higher than the theoretical value
254 for the rutile phase. For the TiO₂-CoN0.25 thin film, the indirect band gap shows values
255 close to those of the indirect band gap of the TiO₂ film with a slight decrease. For the di-
256 rect band gap, two energy levels can be displayed. The first energy level (2.73 eV) is close
257 to the value of the cobalt oxide band gap, while the second energy level (3.54 eV) is close
258 to the theoretical value for the rutile phase. Therefore, the band gaps of the three crystal-
259 line phases present in TiO₂-CoN0.25-GC can be effectively observed. Finally, the
260 TiO₂-CoN0.5-GC film has a band gap value of 3.11 eV, which is close to that of the rutile
261 phase, which is not the dominant phase in this material (A: 37% - R: 33% - S: 30%).
262

263 It is therefore difficult to attribute this value to either phase, rutile or spinel. How-
264 ever, given the previous values found for the rutile phase (3.37 eV and 3.54 eV) and for
265 the spinel phase (2.73 eV), we can imagine that the value of 3.11 eV is an intermediate
266 value that is effectively representative of the band gap of this material. In this type of thin

film (with a high cobalt content), no reliable values for the indirect band gap of the anatase phase could be obtained. Finally, calculations of band gap values from Tauc diagrams confirm the presence of the different crystalline phases and the effect of cobalt oxide: the addition of cobalt oxide to the materials would lower the band gap energy and thus shift the absorption of the materials into the visible region.

2.4. Electronic Properties

In order to compare the electronic conductivity of thin films at the nanometer scale, current measurements were made at negative voltages using C-AFM. For an n-type semiconductor such as TiO_2 , the current flows best at negative voltages, and conversely for a p-type semiconductor such as Co_3O_4 , the current flows best at positive voltages. However, the position of the energy levels of the band structure of the semiconductor in relation to the Fermi level of the metal forming the tip (here PtSi) also has an effect on the current collected. The choice of negative or positive voltage does not necessarily define the nature of the majority carriers, n or p. In our case, it is more relevant to present the results for a negative voltage, since the films mostly contain TiO_2 .

In the topography maps in **Figure 7.a,b,c** the presence of cobalt oxide seems to induce a smoothing of the thin films with a decrease in crystallite aggregation.

Figure 7.d,e,f represents the corresponding current, the distribution is heterogeneous for all the samples, as can be seen from the current maps with two different colors. The percentage of conductive area for the hybrid thin films increases from 20% for TiO_2 -GC to 85% and 98% for TiO_2 -CoN0.25-GC and TiO_2 -CoN0.5-GC, respectively (**Table S3**).

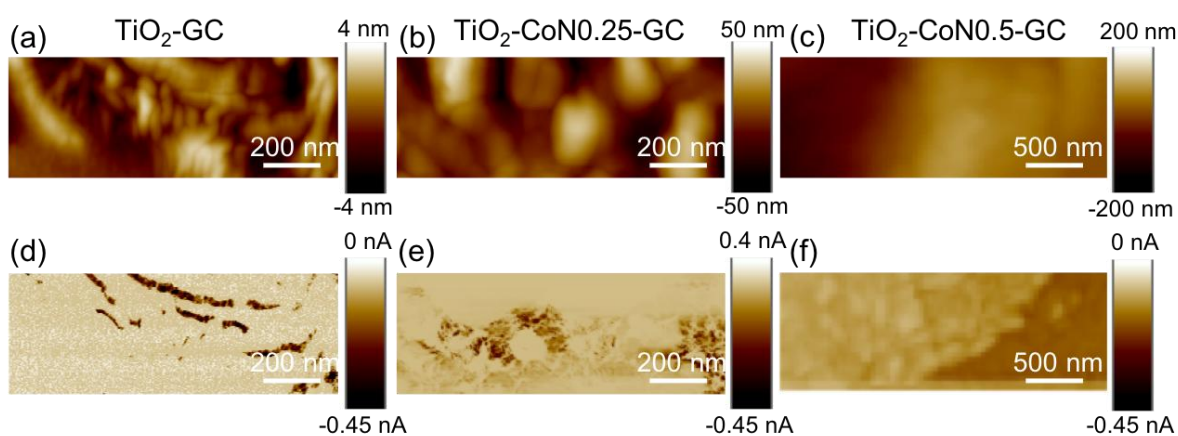


Figure 7. (a, b and c) Topography and (d, e and f) current maps for the corresponding areas below for TiO_2 -GC samples at -5 V, TiO_2 -CoN0.25-GC at -9 V and TiO_2 -CoN0.5-GC at -9 V respectively.

In contrast to the percentage of conductive area, the collected current in the conductive area (i.e. dark area) decreases with the Co ratio ranging from -0.45 nA for TiO_2 -GC to -0.035 nA for TiO_2 -CoN,0.25 and to -0.045 nA/-0.122 nA for TiO_2 -CoN0.5-GC. As it can be seen, for the thin film with the highest cobalt ratio, two current values are collected, proving the inhomogeneous current distribution in the bulk. This could be evidence of the presence of a large aggregate of TiO_2 and Co_3O_4 nanoparticles, with the most conductive areas associated with cobalt oxide, which is known to have better electrical conductivity than titanium oxide. Since the conductive surface and the current collected in the conductive surface exhibit different behavior with Co ratio, it is important to compare the average current over similar surfaces. This mean current ranges from -71 pA for TiO_2 to -28 pA and -47 pA for 0.25 and 0.5 Co ratio respectively. Thus, the presence of cobalt oxide does not have the expected effect on the electronic conductivities

from a nanometric point of view. In fact, Co_3O_4 has a higher intrinsic conductivity than TiO_2 . However, this effect was limited by other parameters such as (i) the reduction of the crystallite sizes, (ii) the modification of the ratio between anatase and rutile phases or the modification of the band gap.

With the aim of studying the electronic conductivity at thin film/electrolyte interface, the electrical model corresponding to our system consists of one resistor R_s connected in series with two resistor-CPE pairs ($R_{p-1}/\text{CPE-p-1}$ and $R_{p-2}/\text{CPE-p-2}$) connected in parallel [44].

The resistor R_s is characteristic of the electrolyte and the two pairs $R_{p-1}/\text{CPE-p-1}$ and $R_{p-2}/\text{CPE-p-2}$ correspond to the ITO support and the supported thin film, respectively. These components are shown in **Figure 8.a**, using a Nyquist plot as example.

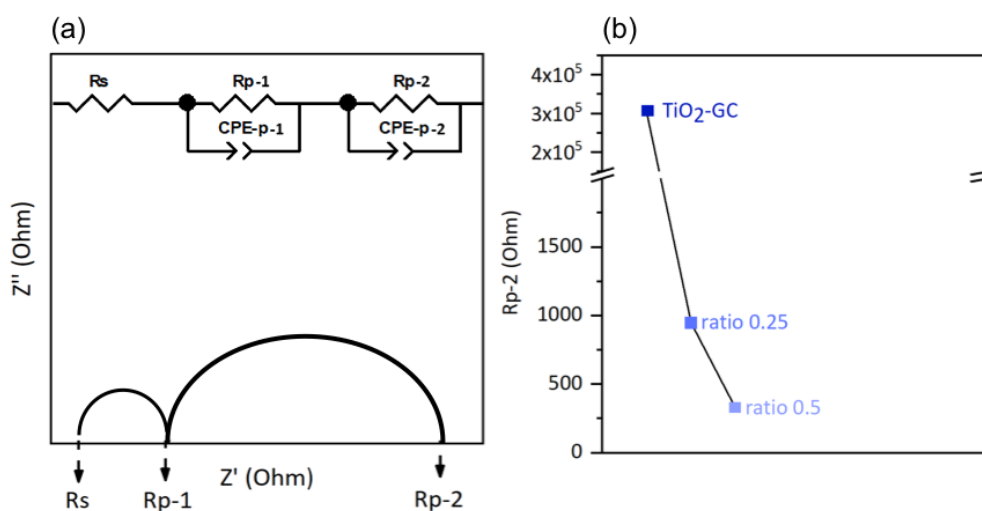


Figure 8. (a) Example of a Nyquist plot and illustration of the equivalent circuit model used in this study; $Z' = \text{Re}Z$ and $Z'' = -\text{Im}Z$ and (b) charge transfer resistance R_{p-2} .

The charge transfer resistances of the electrolyte (R_s) and at the ITO-substrate interface (R_{p-1}) are not expected to vary from sample to sample because the electrolyte and ITO substrate are the same for all samples.

However, the ITO/thin film interface may slightly affect the R_{p-1} value depending on the nature of the thin film in question. The values of R_s and R_{p-1} obtained from the Nyquist plots in the dark are listed in **Table S4**. Differences in these values depending on the nature of the studied thin film are observed without being able to explain them. However, we mainly discuss here the charge transfer resistance at the thin film/electrolyte interface (R_{p-2}) and its evolution according to the nature of the thin films. The lower the R_{p-2} resistance, the easier the electron transfer at the material/electrolyte interface, which generally leads to a better electron transfer in the whole electrochemical cell, for a higher faradic efficiency. The onset potential used for the EIS is the minimum potential required to initiate the electrolysis reaction of water. The values of the onset potentials chosen in this study are derived from the cyclic voltammetry curves presented in the following section and are listed in **Table S4**. The Nyquist plot of the different samples is shown in **Figure S4**, the decrease of the circular arc with the addition of cobalt oxide is obvious. The R_{p-2} resistance value is shown in **Figure 8.b** for better visualization. For the $\text{TiO}_2\text{-GC}$, the R_{p-2} value is 306 771 Ω , which is much higher than that of $\text{TiO}_2\text{-CoN}0.25$ (954 Ω) and $\text{TiO}_2\text{-CoN}0.5$ (332 Ω). The decrease in R_{p-2} is less obvious when the amount of cobalt oxide is increased, but is still visible.

It can be concluded that the presence of cobalt oxide and the increase in specific surface is a great asset to reduce the charge transfer resistance of the hybrid thin films.

2.5. Photoelectrochemical Properties

To study the photoelectrocatalytic performance of thin films, we focused on three characteristics: the onset potential (E_{onset}), the maximum current intensity (I_{max}) and the photocatalytic activity of the materials. **Figure 9** illustrates the voltammograms collected under xenon irradiation for the three thin films.

The onset potential is defined as the voltage at which the water oxidation reaction initiates, theoretically equivalent to 1.23 V. In practice, this potential can range from 1.8 V to 2.7 V due to cathodic and anodic overvoltages and ohmic losses. The reaction requires less energy as the potential decreases. In this case, the introduction of CO_3O_4 decreases the potential significantly, lowering it from 1.84 V in the TiO_2 thin film to 1.62 V in both the $\text{TiO}_2\text{-CoN0.25}$ and $\text{TiO}_2\text{-CoN0.5}$ composite films.

For the maximum current intensities collected at 2 V, we can see a considerable improvement with the presence of cobalt: as the cobalt ratio increases, the current rises from $0.041 \text{ mA}\cdot\text{cm}^{-2}$ for TiO_2 to $0.529 \text{ mA}\cdot\text{cm}^{-2}$ for the 0.25 ratio, then to $1.570 \text{ mA}\cdot\text{cm}^{-2}$ for the 0.5 ratio.

To determine the photocatalytic activity of the thin films, we measured the difference in current intensity between the dark and xenon irradiation. The TiO_2 layer displayed a difference of $0.012 \text{ mA}\cdot\text{cm}^{-2}$, while $\text{TiO}_2\text{-CoN0.25}$ and $\text{TiO}_2\text{-CoN0.5}$ exhibited differences of 0.025 and 0.004, respectively. Based on the relative magnitudes of the current intensities, only TiO_2 demonstrated significant photocatalytic activity. The presence of CO_3O_4 appears to interfere with the photocatalytic capabilities of TiO_2 .

In conclusion, the addition of cobalt and creation of composite thin films have greatly improved the thermodynamic (E_{onset}) and kinetic (I_{max}) aspects of the water oxidation reaction. This enhancement comes at the detriment of TiO_2 photoactivity.

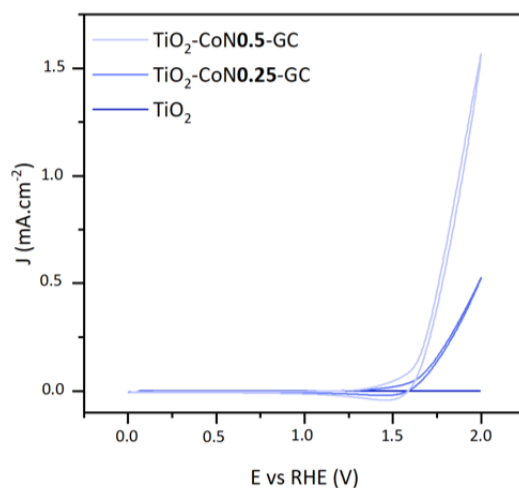


Figure 9. Cyclic voltammetry curves of the three thin film under xenon irradiation.

The stability of the thin films was examined using photocurrent measurements. The stability of the top-performing $\text{TiO}_2\text{-CoN0.5}$ sample is shown in **Figure 10**. The chosen potential is the onset potential + 0.2V to ensure that non-negligible currents are obtained. At this potential, the thin film current density is stable at about $0.85 \text{ mA}\cdot\text{cm}^{-2}$ under xenon irradiation for 3 hours. From this curve, the theoretical amount of hydrogen produced n can be determined by utilizing Faraday's law (5).

In this equation, the electric charge Q is the electric intensity $i(t)$ integrated as a function of time t , n_{e^-} represents the number of electrons involved in the H_2 reduction reaction, and F refers to Faraday's constant. A theoretical yield of $0.3 \mu\text{mol}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ was calculated for the $\text{TiO}_2\text{-CoN}0.5$.

$$n = \frac{\int_0^t i(t) dt}{n_{e^-} \times F} = \frac{Q}{n_{e^-} \times F} \quad (5)$$

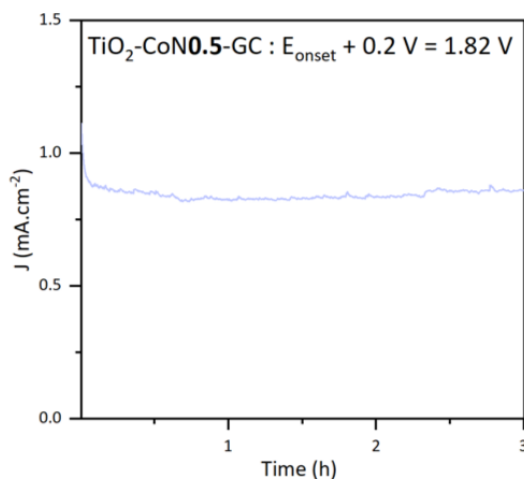


Figure 10. Photocurrent curve of the $\text{TiO}_2\text{-CoN}0.5$ thin film.

3. Conclusion

The synthesis of $\text{TiO}_2\text{-Co}_3\text{O}_4/\text{Co}(\text{OH})_2$ hybrid materials by the sol-gel method has made it possible to highlight the effect of cobalt on the properties of TiO_2 thin films. First, in terms of structural and textural properties, an inversion of the dominance of the anatase and rutile phases in TiO_2 powders before and after the addition of cobalt oxide was observed: the rutile phase was dominant in the absence of cobalt, whereas it was the anatase phase in the presence of cobalt. A homogenization of crystallite and pore size and an increase in specific surface area for hybrid powders were also observed. Secondly, by optical characterization of the thin films using UV-Vis-NIR spectroscopy, it was shown that an increase in the visible absorption of the thin films is possible with the addition of cobalt oxide, and increasingly so with increasing Co/Ti ratio. Finally, the electronic properties of the thin films were characterized in two different ways: by C-AFM (at the nanoscale for volume analysis) and by EIS (at the macroscale for surface analysis). These analyses confirmed the heterogeneity of the electrical properties of the hybrid thin films due to the incorporation of the cobalt oxide. Co_3O_4 in the bulk does not improve the electrical conductivity of the materials, while $\text{Co}(\text{OH})_2$ on the surface of the films induces a significant decrease in the charge transfer resistance. Finally, the presence of cobalt enhances the photoelectrocatalytic properties of composite thin films. The current density of cobalt-free thin films increases by a factor of 30, resulting in a maximum current of $1.570 \text{ mA}\cdot\text{cm}^{-2}$ at 2V for the $\text{TiO}_2\text{-CoN}0.5$ thin film with the highest Ti/Co ratio. The thin film's stability is demonstrated for 3 hours under xenon illumination, enabling it to theoretically produce $0.3 \mu\text{mol}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ of H_2 .

413 Given the feasibility of this synthesis method, it is possible to explore the use of
414 other metal oxide types, such as BiVO₄ or Fe₂O₃, in sol-gel one-pot synthesis to investigate
415 the advantages of such a heterojunction. Additionally, future work will focus on cou-
416 pling real-time H₂ production with the photodegradation of a model pollutant in the
417 electrolyte to qualify these materials as photoanodes for a PEC cell operating with water
418 from real effluents.

419 4. Experimental Section

420 4.1. Synthesis procedure

421 The starting materials, titanium (IV) isopropoxyde (TTIP, 99.999 % trace metal ba-
422 sis), cobalt nitrate hexahydrate (Co(NO₃)₂•6 H₂O, ≥ 98%), and nitric acid (HNO₃, ACS
423 reagent 70%) were all purchased from Sigma Aldrich. The three different polymeric
424 biosurfactants are the same as those used in our previous work[35]: GBACoco (lot PF345,
425 Surfactgreen, France – named GC), GBAC18:1 (lot PF339, Surfactgreen, France – named
426 GB) and Lansperse BIO868 (Bio-Loop Technology, Lankem, United Kingdom – named
427 BIO). They are all bio-based and 100 % renewable. The solutions were prepared by a
428 sol-gel method; for TiO₂, 10 mL of TTIP was mixed with 16.85 mL of HNO₃ (2 mol.L⁻¹),
429 and for TiO₂-Co₃O₄, the cobalt nitrate was further added in two different molar ratios
430 (HNO₃/TTIP/Co(NO₃)₂•6 H₂O = 1/1/0.25 and 1/1/0.5). Once the solution was stabilized, 1
431 g of surfactant was added. Then, the samples were shaped in two different forms: as
432 powders for structural and morphological characterization and as thin films for the other
433 characterizations. The details of the dip coating, drying and calcination steps have been
434 reported in previous paper.^[32] Samples with ratios of 1/1/0.25 and 1/1/0.5 are hereafter
435 referred to as TiO₂-CoN0.25 and TiO₂-CoN0.5, respectively.

436 4.2. Materials characterizations

437 4.2.1. Structural characterization

438 Powder X-ray Diffraction (XRD) was performed using a X'pert Pro (Pan Analytical)
439 diffractometer with Cu-K α radiation (K α 1 1.5405980 Å, K α 2 1.5444260 Å, ratio K α 1/K α 2
440 1.05) operating at 40 kV and 20 mA. Diffraction patterns were collected from 20° to 60°
441 with a step size of 0.008° and a scan rate of 0.013° per second. Rietveld refinement was
442 performed using FullProf with CIF file of anatase phase (CollCode 92363 - Weirich T.E -
443 2000), rutile phase (CollCode 93097 - Ballirano P - 2001) and spinel phase (CollCode
444 290720 - Meena P.L - 2013). The BET (Brunauer, Emmet and Teller) specific surface area
445 and mean pore size of the powders were measured using a Micromeritics ASAP-2010.

446 4.2.2. Morphological and chemical characterization

447 XPS analysis was performed on an ESCALAB 250 (Thermo Electron) using a mon-
448 ochromatic source, Al K α , as the excitation source and photoelectron spectra were cali-
449 brated as the binding energy relative to the energy of C-C of C1s at 284.8 eV. The relative
450 error of the XPS atomic percentages is 10%. The thickness and surface area of the thin
451 films were observed on a Hitachi S4800 with an AztecOne energy dispersive spectrome-
452 ter. The error of the estimated thickness measurement and EDX ratio is 10-20%.

453 4.2.3. Optical and electrical characterization

454 UV absorption and band gap of the thin films were investigated using an integrating
455 sphere spectrophotometer Shimadzu UV 3600. Nanoscale conductive analysis of the thin
456 films was performed on a Bruker Multimode 8 Atomic Force Microscope (AFM) setup
457 equipped with a PtSi tip (radius of curvature R_c = 27 nm and spring constant k = 1.8
458 N.m⁻¹) using the conductive AFM (C-AFM) mode. A contact force of 33 nN and a current
459 sensitivity module of
460 100 nA.V⁻¹ were applied. The current was probed over a 2 μm × 0.5 μm area at three dif-

ferent locations on each sample with good consistency. A 384 x 96 pixel matrix was used for imaging, giving a pixel size of 5.2 nm x 5.2 nm.

4.2.4. Photo-Electrochemical characterizations

Cyclic voltammetry and photocurrent experiments were monitored on a Solartron SI 1287 and impedance spectroscopy on a Solartron SI 1260. The photoelectrochemical cell was supplied by Pine Research Co USA and was equipped with a quartz window. The electrolyte was a solution of 0.01 mol.L⁻¹ NaOH - 0.1 mol.L⁻¹ Na₂SO₄ and the Ag/AgCl electrode was used as the reference electrode and glass carbon as the counter electrode. Cyclic voltammetry curves were measured from 0.0 V/RHE to 2.0 V/RHE at a scan rate of 50 mV.s⁻¹. The stability of the thin films was investigated by applying the onset potential + 0.2 V for 3 hours. The interfacial conductivity of the thin films was measured in the dark at the onset potential over the frequency range from 0.1 Hz to 106 Hz using an AC voltage of 10 mV amplitude.

A 75 W LOT Quantum Design xenon lamp with a wavelength range of 250-2700 nm and a power density of 3 mW.cm⁻² was used for the illumination.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: BET results with p/p₀ being the ratio of the applied N₂ pressure over the N₂ relative vapor pressure. (i) Isotherm of GC samples, (ii) Isotherm of GB samples and (iii) Isotherm of BIO samples; Figure S2: Pore size distribution for the TiO₂-CoN0.25 samples, (i) TiO₂-CoN0.25-GC, (ii) TiO₂-CoN0.25-GB and (iii) TiO₂-CoN0.25-BIO; Figure S3: Pore size distribution for the TiO₂-CoN0.5 samples, (i) TiO₂-CoN0.5-GC, (ii) TiO₂-CoN0.5-GB and (iii) TiO₂-CoN0.5-BIO; Figure S4: Nyquist plot in the dark at the onset potential for (i) TiO₂-GC (ii) TiO₂-CoN0.25-GC and (iii) TiO₂-CoN0.5-GC; Table S1: Rietveld refinement data; Table 2: Crystallite size by Scherrer formula; Table S3: Results from C-AFM characterisation; Table S4: Data from the electrochemical impedance spectroscopy.

Author Contributions: F.D. performed the experiments, analyzed the data, discussed the results, and drafted and revised the manuscript. V.F. performed XPS experiments, discussed the related results and revised the manuscript. C.V.-F. performed C-AFM experiments, discussed the related results and revised the manuscript. M.R., F.R., and S.R. discussed the results, drafted and revised the manuscript, and oversaw and validated the work. All authors have read and approved to the published version of the manuscript.

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