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# 2 Hybrid photoelectrocatalytic TiO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/Co(OH)<sub>2</sub> 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 TiO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/Co(OH)<sub>2</sub> photoanodes prepared by  
17 the sol-gel method using biosurfactants are currently being developed in our group. The combina-  
18 tion of the TiO<sub>2</sub> 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 TiO<sub>2</sub>-Co<sub>0.5</sub> sample achieving a current of 1.570 mA.cm<sup>-2</sup> and a  
23 theoretical H<sub>2</sub> production rate of 0.3 μmol.min<sup>-1</sup>.cm<sup>-2</sup> under xenon illumination.

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

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## 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 TiO<sub>2</sub>, already known for  
41 its photocatalytic properties, among other advantages [9–11]. However, TiO<sub>2</sub> 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 TiO<sub>2</sub> semiconductor with a p-type semiconductor

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45 can improve these properties [15–18]. Cobalt oxide has already proven itself as a dopant  
46 for TiO<sub>2</sub> 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]. Co<sub>3</sub>O<sub>4</sub> 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-TiO<sub>2</sub> | p-Co<sub>3</sub>O<sub>4</sub> type heterojunction.

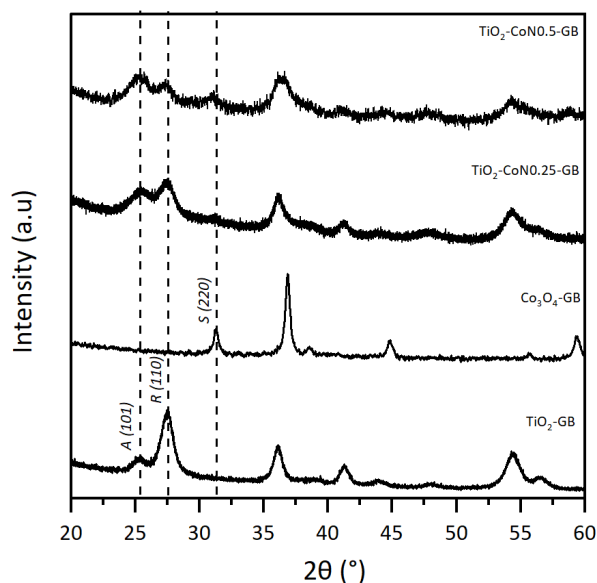
52 This kind of heterojunction has demonstrated enhanced electrochemical perfor-  
53 mance through diverse synthesis routes such as hydrothermal route [26,27], anodization  
54 [28], atomic layer deposition [29], metal organic chemical vapor deposition [30], im-  
55 pregnation [31]. Regarding the sol-gel 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 (HNO<sub>3</sub>/TTIP/Co(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O = 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

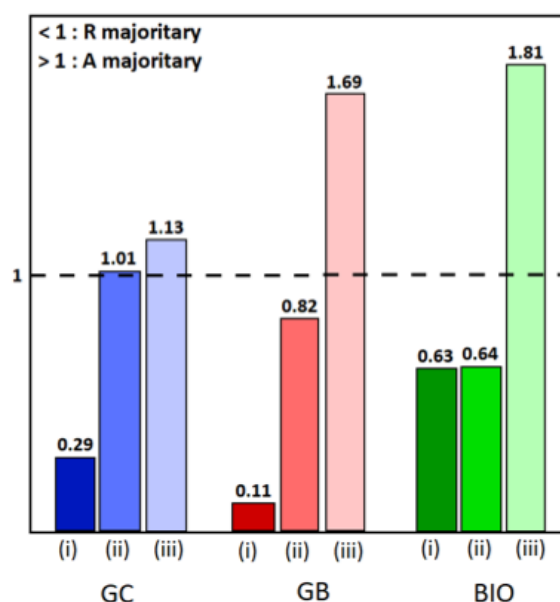
67 TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> samples prepared with the GB surfactant were selected to illustrate the  
68 XRD powder results in **Figure 1** with the diffractograms of TiO<sub>2</sub>-GB, TiO<sub>2</sub>-CoN0.25-GB,  
69 TiO<sub>2</sub>-CoN0.5-GB and Co<sub>3</sub>O<sub>4</sub>-GB. In order to compare the crystal structures of the  
70 TiO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> hybrid powders with those of the individual oxides, a Co<sub>3</sub>O<sub>4</sub> powder (1:1:1  
71 ratio) was synthesized using the same procedure as described above. On the TiO<sub>2</sub>-GB  
72 diffractogram, the presence of TiO<sub>2</sub> 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 Co<sub>3</sub>O<sub>4</sub>-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 Co<sub>3</sub>O<sub>4</sub> peaks in the composite materials diffractograms  
80 (TiO<sub>2</sub>-CoN0.25-GB and TiO<sub>2</sub>-CoN0.5-GB). However, the three phases of the hybrid  
81 powder are observable, and it is seen that the addition of Co<sub>3</sub>O<sub>4</sub> does not affect the posi-  
82 tion of the diffracted TiO<sub>2</sub> peaks, but does appear to affect the anatase/rutile phase ratio.



83  
84 **Figure 1.** Powder diffraction patterns for TiO<sub>2</sub>-GB, CO<sub>3</sub>O<sub>4</sub>-GB, TiO<sub>2</sub>-CoN0.25-GB, and TiO<sub>2</sub>-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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 Co<sub>3</sub>O<sub>4</sub> 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 TiO<sub>2</sub> type samples, (ii) for TiO<sub>2</sub>-CoN0.25 type samples and, (iii) for  
98 TiO<sub>2</sub>-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),  $\lambda$  as the CuK $\alpha$  wavelength

(in nanometers), HW as the half-width value (in radians), and  $\theta$  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 TiO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> phase mixture allows a smoothing of the crystallite size of the different TiO<sub>2</sub> 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 TiO<sub>2</sub>-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 TiO<sub>2</sub> powders and increases with the amount of cobalt oxide. In fact, we find the following hierarchy TiO<sub>2</sub>-CoN0.5 > TiO<sub>2</sub>-CoN0.25 > TiO<sub>2</sub> 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 m<sup>2</sup>.g<sup>-1</sup> 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 m<sup>2</sup>.g<sup>-1</sup> 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 TiO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> 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.

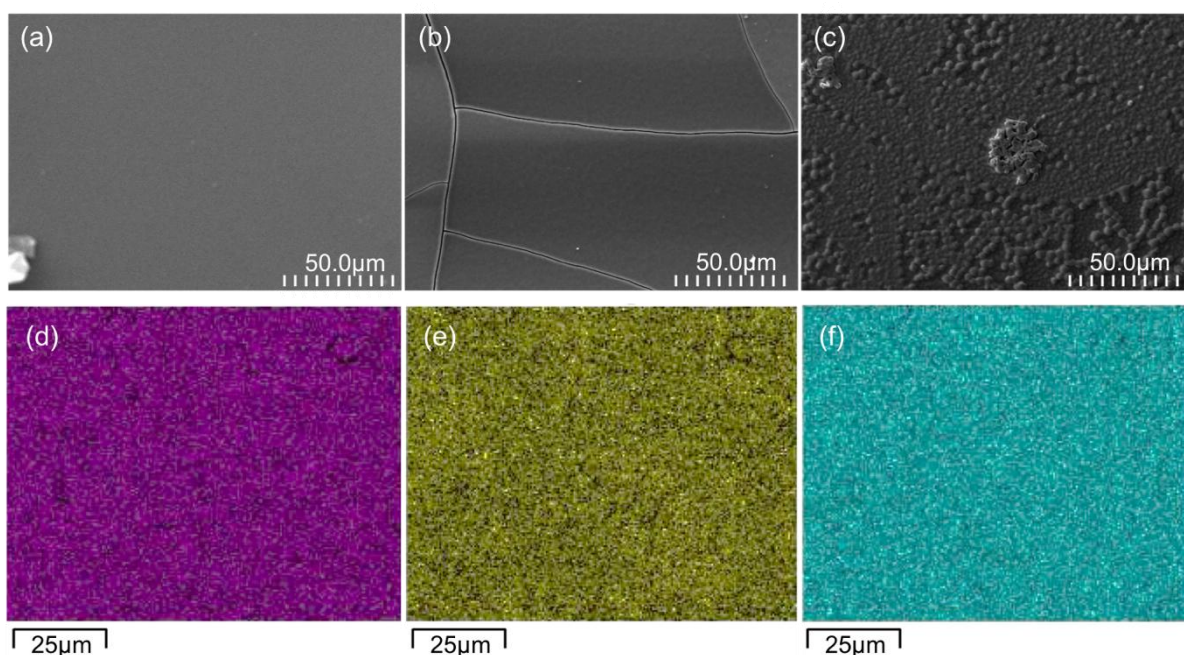
Samples	BET surface area (m <sup>2</sup> /g)	Adsorption Average Pore Width (nm)	BET Pore size distribution (nm)
TiO <sub>2</sub> -GC	101	2.66	Bimodal: 4 nm - 11 nm
TiO <sub>2</sub> -CoN0.25-GC	112	4.85	Bimodal: 3.5 nm - 5 nm
TiO <sub>2</sub> -CoN0.5-GC	126	4.27	Unimodal: 3.5 nm
TiO <sub>2</sub> -GB	31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

The pore size distribution for the TiO<sub>2</sub>-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 TiO<sub>2</sub>-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  $\text{Co}_3\text{O}_4$ . 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

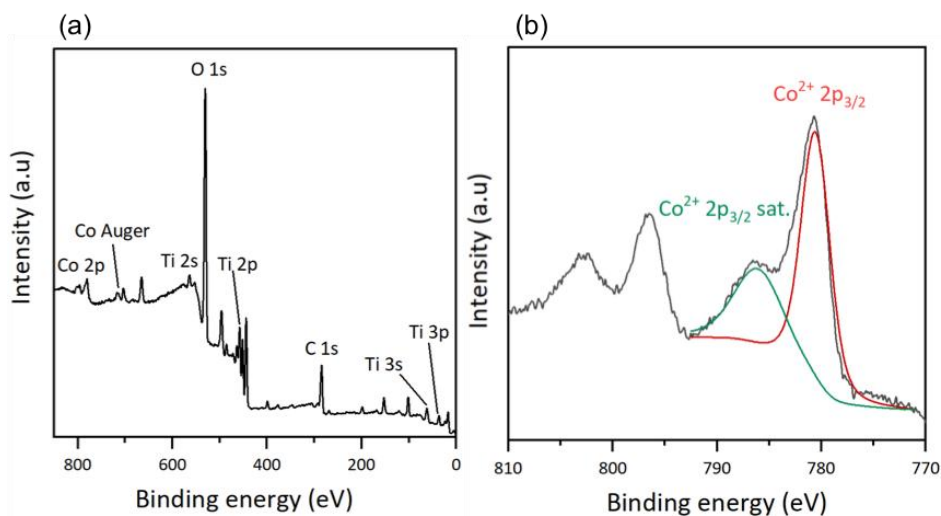
158 On the other hand, when the ratio is increased to 0.5 (**Figure 3.c**), the appearance of  
159 the thin film surface is completely changed. A surface consisting of aggregates of  $\text{TiO}_2$   
160 and  $\text{Co}_3\text{O}_4$  nanoparticles is observed. This was confirmed by a  $5\ \mu\text{m} \times 5\ \mu\text{m}$  surface to-  
161 pography measurement by AFM (not shown) which demonstrated an increase in the  
162 arithmetic surface roughness from 0.8 nm for  $\text{TiO}_2$  to 3.8 nm and 11.5 nm for  $\text{Co}_3\text{O}_4$  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  $1100 \pm 350$  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  $\text{TiO}_2$  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 TiO<sub>2</sub>-CoN0.5-GC, (b) Co2p scan after deconvolution of TiO<sub>2</sub>-CoN0.5-GC.

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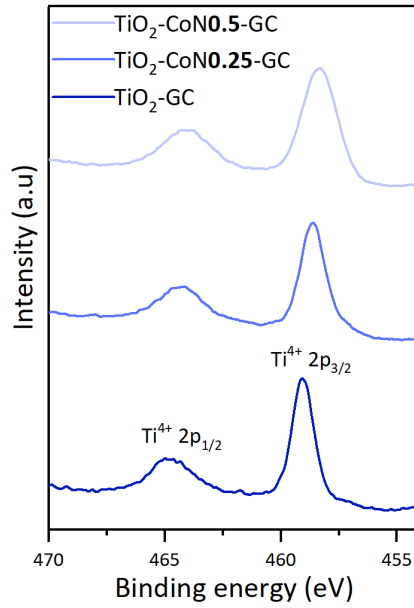
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To verify the nature of the cobalt on the surface of the thin films, a high-resolution deconvolution of the Co 2p spectrum was performed (**Figure 4.b**). A main peak related to Co<sup>2+</sup> 2p<sub>3/2</sub> at 780.5 eV and its satellite peak at 786.0 eV can be identified. The presence of a satellite peak is characteristic of the Co<sup>2+</sup>, 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 Co<sub>3</sub>O<sub>4</sub> is a mixed valence compound, cobalt exists in two oxidation states: Co<sup>2+</sup> and Co<sup>3+</sup>. However, the deconvolution shows only the presence of Co<sup>2+</sup>, 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 Co<sup>2+</sup> 2p<sub>3/2</sub> peak indicates the presence of cobalt in the form of Co(OH)<sub>2</sub>[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**.

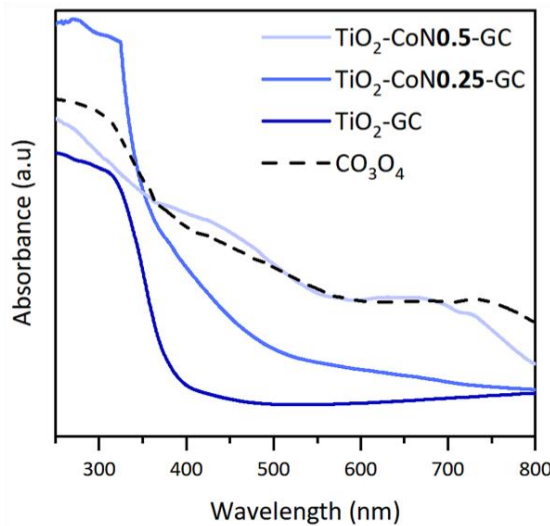


199  
200 **Figure 5.** Comparison of Ti 2p scan of the three thin films.

201  
202 The Ti 2p spectra display two symmetrical peaks corresponding to Ti 2p<sub>1/2</sub> and Ti  
203 2p<sub>3/2</sub>, representing Ti<sup>4+</sup> in TiO<sub>2</sub>. With the incorporation of Co, there is a subsequent shift to  
204 lower binding energies (+0.5 eV for TiO<sub>2</sub>-CoN0.25 and 0.2 eV for TiO<sub>2</sub>-CoN0.5), indicating  
205 the occurrence of electron transfer between Co<sub>3</sub>O<sub>4</sub>/Co(OH)<sub>2</sub> and TiO<sub>2</sub>. 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. TiO<sub>2</sub> is an oxide that absorbs mainly in the  
212 UV region (from 100 to 400 nm), while Co<sub>3</sub>O<sub>4</sub> absorbs in the visible region (from 400 to  
213 780 nm). **Figure 6** shows the absorption spectra of the samples. The TiO<sub>2</sub> thin film spec-  
214 trum is characteristic of TiO<sub>2</sub> 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 Co<sub>3</sub>O<sub>4</sub>.

220 The absorption spectrum of the TiO<sub>2</sub>-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 TiO<sub>2</sub>-CoN0.25 and TiO<sub>2</sub>-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 TiO<sub>2</sub>-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  $\alpha$  (cm<sup>-1</sup>) and the frequency  $\nu$  (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<sup>-1</sup>), and  $\lambda$  is the wavelength (m).

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

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

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

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

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

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

261  
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

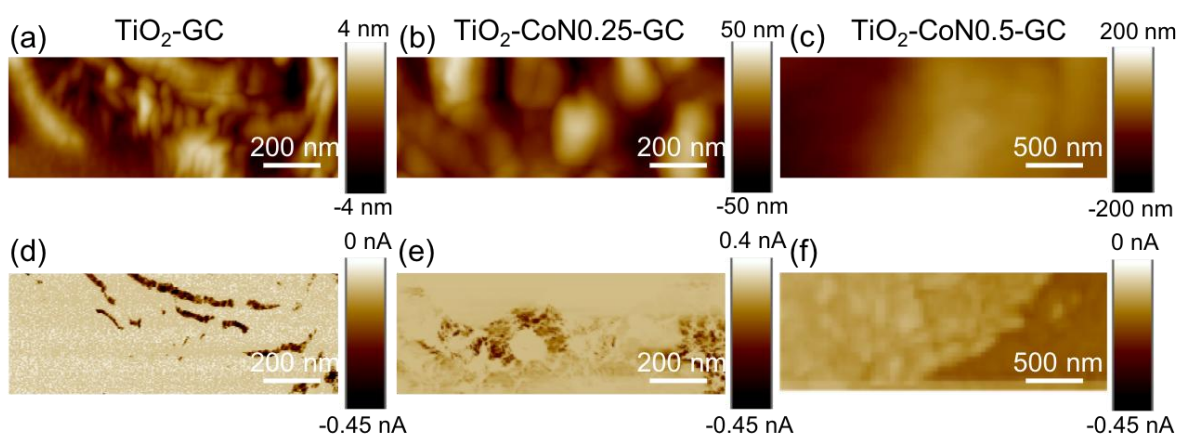
267 film (with a high cobalt content), no reliable values for the indirect band gap of the  
268 anatase phase could be obtained. Finally, calculations of band gap values from Tauc di-  
269 agrams confirm the presence of the different crystalline phases and the effect of cobalt  
270 oxide: the addition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

#### 272 2.4. Electronic Properties

273  
274 In order to compare the electronic conductivity of thin films at the nanometer scale,  
275 current measurements were made at negative voltages using C-AFM. For an n-type  
276 semiconductor such as  $\text{TiO}_2$ , the current flows best at negative voltages, and conversely  
277 for a p-type semiconductor such as  $\text{Co}_3\text{O}_4$ , the current flows best at positive voltages.  
278 However, the position of the energy levels of the band structure of the semiconductor in  
279 relation to the Fermi level of the metal forming the tip (here PtSi) also has an effect on the  
280 current collected. The choice of negative or positive voltage does not necessarily define  
281 the nature of the majority carriers, n or p. In our case, it is more relevant to present the  
282 results for a negative voltage, since the films mostly contain  $\text{TiO}_2$ .

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

285 **Figure 7.d,e,f** represents the corresponding current, the distribution is heterogene-  
286 ous for all the samples, as can be seen from the current maps with two different colors.  
287 The percentage of conductive area for the hybrid thin films increases from 20% for  
288  $\text{TiO}_2\text{-GC}$  to 85% and 98% for  $\text{TiO}_2\text{-CoN0.25-GC}$  and  $\text{TiO}_2\text{-CoN0.5-GC}$ , respectively (**Table**  
289 **S3**).  
290



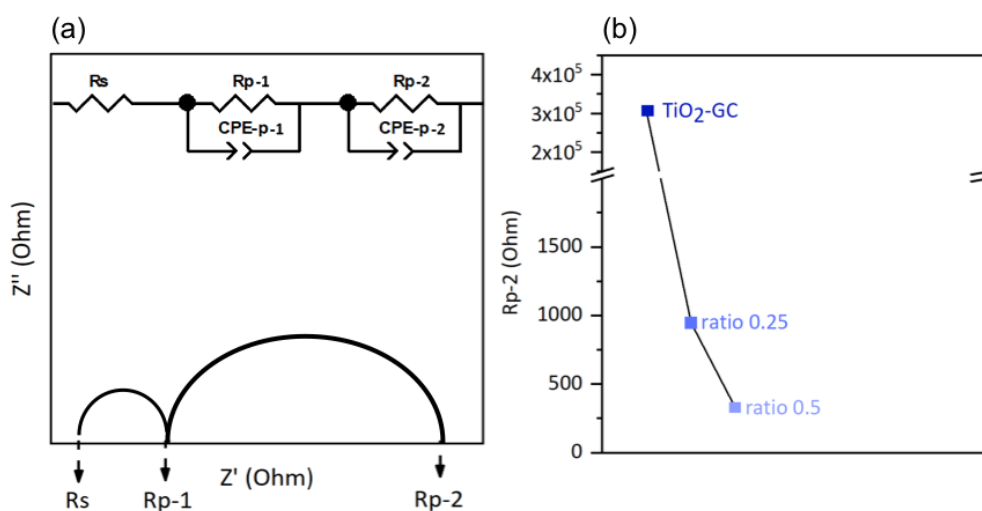
291  
292 **Figure 7.** (a, b and c) Topography and (d, e and f) current maps for the corresponding areas below for  $\text{TiO}_2\text{-GC}$   
293 samples at -5 V,  $\text{TiO}_2\text{-CoN0.25-GC}$  at -9 V and  $\text{TiO}_2\text{-CoN0.5-GC}$  at -9 V respectively.

294  
295 In contrast to the percentage of conductive area, the collected current in the con-  
296 ductive area (i.e. dark area) decreases with the Co ratio ranging from -0.45 nA for  
297  $\text{TiO}_2\text{-GC}$  to -0.035 nA for  $\text{TiO}_2\text{-CoN},0.25$  and to -0.045 nA/-0.122 nA for  $\text{TiO}_2\text{-CoN0.5-GC}$ .  
298 As it can be seen, for the thin film with the highest cobalt ratio, two current values are  
299 collected, proving the inhomogeneous current distribution in the bulk. This could be  
300 evidence of the presence of a large aggregate of  $\text{TiO}_2$  and  $\text{Co}_3\text{O}_4$  nanoparticles, with the  
301 most conductive areas associated with cobalt oxide, which is known to have better elec-  
302 trical conductivity than titanium oxide. Since the conductive surface and the current  
303 collected in the conductive surface exhibit different behavior with Co ratio, it is im-  
304 portant to compare the average current over similar surfaces. This mean current ranges  
305 from -71 pA for  $\text{TiO}_2$  to -28 pA and -47 pA for 0.25 and 0.5 Co ratio respectively. Thus, the  
306 presence of cobalt oxide does not have the expected effect on the electronic conductivities

from a nanometric point of view. In fact,  $\text{Co}_3\text{O}_4$  has a higher intrinsic conductivity than  $\text{TiO}_2$ . 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  $\Omega$ , which is much higher than that of  $\text{TiO}_2\text{-CoN}0.25$  (954  $\Omega$ ) and  $\text{TiO}_2\text{-CoN}0.5$  (332  $\Omega$ ). 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

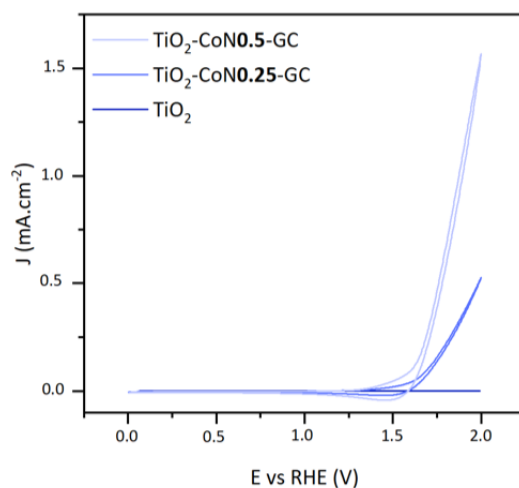
To study the photoelectrocatalytic performance of thin films, we focused on three characteristics: the onset potential ( $E_{\text{onset}}$ ), the maximum current intensity ( $I_{\text{max}}$ ) and the photocatalytic activity of the materials. **Figure 9** illustrates the voltammograms collected under 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  $\text{CO}_3\text{O}_4$  decreases the potential significantly, lowering it from 1.84 V in the  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  demonstrated significant photocatalytic activity. The presence of  $\text{CO}_3\text{O}_4$  appears to interfere with the photocatalytic capabilities of  $\text{TiO}_2$ .

In conclusion, the addition of cobalt and creation of composite thin films have greatly improved the thermodynamic ( $E_{\text{onset}}$ ) and kinetic ( $I_{\text{max}}$ ) aspects of the water oxidation reaction. This enhancement comes at the detriment of  $\text{TiO}_2$  photoactivity.

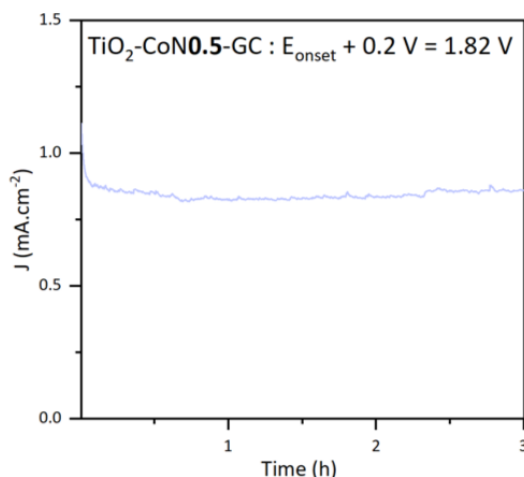


**Figure 9.** Cyclic voltammetry curves of the three thin film under xenon irradiation.

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  $\text{TiO}_2$  thin films. First, in terms of structural and textural properties, an inversion of the dominance of the anatase and rutile phases in  $\text{TiO}_2$  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.  $\text{Co}_3\text{O}_4$  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 BiVO<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub>, 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 H<sub>2</sub> 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(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O, ≥ 98%), and nitric acid (HNO<sub>3</sub>, 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 TiO<sub>2</sub>, 10 mL of TTIP was mixed with 16.85 mL of HNO<sub>3</sub> (2 mol.L<sup>-1</sup>),  
429 and for TiO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>, the cobalt nitrate was further added in two different molar ratios  
430 (HNO<sub>3</sub>/TTIP/Co(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O = 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.<sup>[32]</sup> Samples with ratios of 1/1/0.25 and 1/1/0.5 are hereafter  
435 referred to as TiO<sub>2</sub>-CoN0.25 and TiO<sub>2</sub>-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 $\alpha$  radiation (K $\alpha$ 1 1.5405980 Å, K $\alpha$ 2 1.5444260 Å, ratio K $\alpha$ 1/K $\alpha$ 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 $\alpha$ , 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<sub>c</sub> = 27 nm and spring constant k = 1.8  
458 N.m<sup>-1</sup>) using the conductive AFM (C-AFM) mode. A contact force of 33 nN and a current  
459 sensitivity module of  
460 100 nA.V<sup>-1</sup> 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<sup>-1</sup> NaOH - 0.1 mol.L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> 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<sup>-1</sup>. 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<sup>-2</sup> was used for the illumination.

**Supplementary Materials:** The following supporting information can be downloaded at: [www.mdpi.com/xxx/s1](http://www.mdpi.com/xxx/s1), Figure S1: BET results with p/p<sub>0</sub> being the ratio of the applied N<sub>2</sub> pressure over the N<sub>2</sub> 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 TiO<sub>2</sub>-CoN0.25 samples, (i) TiO<sub>2</sub>-CoN0.25-GC, (ii)TiO<sub>2</sub>-CoN0.25-GB and (iii) TiO<sub>2</sub>-CoN0.25-BIO; Figure S3: Pore size distribution for the TiO<sub>2</sub>-CoN0.5 samples, (i) TiO<sub>2</sub>-CoN0.5-GC, (ii) TiO<sub>2</sub>-CoN0.5-GB and (iii) TiO<sub>2</sub>-CoN0.5-BIO; Figure S4: Nyquist plot in the dark at the onset potential for (i) TiO<sub>2</sub>-GC (ii) TiO<sub>2</sub>-CoN0.25-GC and (iii) TiO<sub>2</sub>-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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**Conflicts of Interest:** The authors declare no conflict of interest.

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