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# A direct Z-scheme for the photocatalytic hydrogen production from ethanol dehydrogenation on CoTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures

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#### ABSTRACT

Photocatalytic H<sub>2</sub> evolution from ethanol dehydrogenation is a convenient strategy to store solar energy in a highly valuable fuel with potential zero net CO<sub>2</sub> balance. Herein, we report on the synthesis of CoTiO<sub>3</sub>/TiO<sub>2</sub> composite catalysts with controlled amounts of highly distributed CoTiO<sub>3</sub> nanodomains for photocatalytic ethanol dehydrogenation. We demonstrate these materials to provide outstanding hydrogen evolution rates under UV and visible illumination. The origin of this enhanced activity is extensively analyzed. In contrast to previous assumptions, UV-vis absorption spectra and ultraviolet photoelectron spectroscopy (UPS) prove CoTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures to have a type II band alignment, with the conduction band minimum of  $CoTiO_3$  below the  $H_2/H^+$  energy level. Additional steady-state photoluminescence (PL) spectra, time-resolved PL spectra (TRPLS) and electrochemical characterization prove such heterostructures to result in enlarged life times of the photogenerated charge carriers. These experimental evidences point toward a direct Z-scheme as the mechanism enabling the high photocatalytic activity of CoTiO<sub>3</sub>/TiO<sub>2</sub> composites toward ethanol dehydrogenation. Besides, we probe small changes of temperature to strongly modify the photocatalytic activity of the materials tested, which could be used to further promote performance in a solar thermo-photocatalytic reactor.

**KEYWORDS:** Bioethanol; photocatalysis; hydrogen; titanium dioxide; Z-scheme; titanate, dehydrogenation

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### INTRODUCTION

Hydrogen is regarded as one of the most convenient energy vectors, owing to its abundance, cleanness, and high energy density. However, as there is no natural source of molecular hydrogen, H<sub>2</sub> needs to be produced from chemical compounds such as water, hydrocarbons or alcohols, what requires a supply of energy. Among the possible sources of hydrogen, ethanol is particularly suitable both thermodynamically and in terms of net  $CO_2$  emissions. The production of hydrogen from ethanol is less energetically demanding than from water splitting, and the product can be more easily separate. At the same time, ethanol is the most common liquid fuel derived from biomass, being worldwide produced in huge quantities (~10<sup>11</sup> liters annually) by the fermentation of sugars from corn starch and sugar cane and from large-volume low-value biomass like lignocellulose and organic waste.<sup>1-4</sup> Ethanol biosourcing compensates the  $CO_2$  released during combustion through its capture during photosynthesis, leading to a near zero net  $CO_2$  footprint. Besides, being liquid at ambient temperature, ethanol can be easily stored and transported, to the point that the already stablished infrastructure for ethanol production and distribution makes it a very convenient precursor of other fuels, including H<sub>2</sub> and higher alcohols.<sup>4, 5</sup>

In terms of source of energy, the use of solar energy to generate fuels and particularly hydrogen is especially attractive due to its abundance and ubiquitous availability at zero cost. From another point of view, the production of solar fuels can be regarded as a suitable strategy to store this intermittent form of energy.<sup>6, 7</sup>

Photocatalysts allow the production of molecular hydrogen from ethanol dehydrogenation using solar energy as unique energy input.<sup>1</sup> In the simplest scenario, ethanol can be photocatalytically dehydrogenated at ambient pressure and temperature, yielding molecular hydrogen and acetaldehyde, and releasing no CO<sub>2</sub>:

$$CH_3CH_2OH + 2h^+ \rightarrow CH_3CHO + 2H^+ \tag{1}$$

$$2H^+ + 2e^- \to H_2 \tag{2}$$

Acetaldehyde is a particularly versatile chemical precursor extensively used by the chemical industry because the aldehyde moiety provides a functional handle that, through different reaction pathways, can be used to yield a range of products, including upgraded fuels as well as large volume commodity chemicals such as acetic acid or butadiene, among others.<sup>8-10</sup> Besides, this dehydrogenation reaction is also the limiting step in the synthesis of higher alcohols through the Guerbet reaction. Thus, separating it from the rest of the process could

allow not only saving energy but also improving product selectivity by reducing the process maximum temperature.<sup>4, 11, 12</sup>

To engineer an efficient photocatalyst for solar energy storage into fuels it is necessary to ensure an effective absorbance of the solar radiation, long lasting photogenerated charge carriers, which generally requires a means of charge separation, and a proper surface interaction with all the involved chemical species. To satisfy these demanding requirements, composite materials are generally used to extend the range of spectrum absorption, drive charge separation and offer additional adsorption/reaction sites. In many systems it is found that the photocatalytic reaction is most likely occurring at the interface between two different materials, what makes the engineering of this interface particularly important.<sup>7</sup> To minimize recombination sites and defects, the interphase can be optimized by the direct growth of one phase from the surface of the other, or even more conveniently, by the segregation of nanodomains of the two phases from a common precursor material. To maximize the interface and minimize diffusion and side reactions of the involved species, a nanoscale dispersion of the different phases is required.

Titanium dioxide (TiO<sub>2</sub>) is the prototype photocatalyst due to its outstanding optoelectronic properties, natural abundance, high photocorrosion resilience, lack of toxicity and low cost.<sup>13, 14</sup> However, TiO<sub>2</sub> practical application is hampered by its large bandgap, that limits the range of solar spectra used.<sup>15, 16</sup> The doping of titania with different elements and its combination with light absorbers have been demonstrated effective in extending the range of solar spectrum absorbed. But this improvement generally comes at the cost of decreasing internal quantum efficiencies due to increased charge carrier recombination, resulting in a limited overall improvement of the photon-to-fuel energy conversion efficiency.

Cobalt titanate (CoTiO<sub>3</sub>) is a narrow band gap oxide semiconductor with a ABO<sub>3</sub> perovskite crystal structure, large carrier mobility, excellent stability, and high absorption coefficient.<sup>17-19</sup> In combination with graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) and Pt, it has been recently explored for photocatalytic hydrogen generation through a direct Z-scheme, where holes photogenerated in CoTiO<sub>3</sub> participate in the oxidation reaction, electrons photogenerated in the g-C<sub>3</sub>N<sub>4</sub> drive the reduction reaction, and at the interphase of the two materials electrons photogenerated in CoTiO<sub>3</sub> recombine with holes generated in g-C<sub>3</sub>N<sub>4</sub>.<sup>17</sup> CoTiO<sub>3</sub>/TiO<sub>2</sub> composites have also been synthesized and used in multiple applications, including photoelectrochemical water splitting;<sup>20</sup> photocatalytic dye degradation,<sup>21</sup> oxidative dehydrogenation of cyclohexane;<sup>22</sup> dry reforming of methane;<sup>23</sup> peroxymonosulfate activation

and metronidazole degradation;<sup>24</sup> resistive humidity sensing;<sup>25</sup> electrochemical sensing of dopamine;<sup>26</sup> and anode in lithium ion batteries,<sup>27</sup> but surprisingly CoTiO<sub>3</sub>/TiO<sub>2</sub> composites have not been thoroughly tested as photocatalysts for H<sub>2</sub> production from bioethanol dehydrogenation.

Herein, CoTiO<sub>3</sub>/TiO<sub>2</sub> photocatalysts with different CoTiO<sub>3</sub> amounts are produced by phase segregation during annealing of a Co-doped TiO<sub>2</sub> precursor prepared by hydrothermal reaction. CoTiO<sub>3</sub>/TiO<sub>2</sub> photocatalysts were tested for hydrogen generation from ethanol dehydration in gas phase. A 10% alcohol solution in water was used owing to its optimized activity and its proximity to commercial bioethanol, produced in the form of diluted aqueous solution from biomass fermentation. Notice that using aqueous solutions, thus avoiding the costly ethanol separation and purification, is fundamental for the cost-effectiveness of the process.<sup>2, 3, 5</sup>

#### **RESULTS AND DISCUSSION**

### Photocatalysts Characterization

Cobalt-doped titania (TiO<sub>2</sub>:Co) nanopowders with different Co amounts were obtained by the simultaneous hydrothermal reaction of titanium (IV) isopropoxide and cobalt (II) nitrate at 170 °C for 14 h. XRD patterns of these materials only displayed the anatase TiO<sub>2</sub> crystallographic phase (Figure S2). Co introduction resulted in a shift of the anatase diffraction peaks to lower angles, which indicated the incorporation of Co inside TiO<sub>2</sub> lattice structure. EDX, XPS, ICP analysis showed the TiO<sub>2</sub>:Co nanopowders to contain Co/Ti atomic ratios above the nominal values, which evidenced a better reaction yield of cobalt (II) nitrate than titanium (IV) isopropoxide (Table S1). TEM micrographs (Figures 1b, S6) displayed most TiO<sub>2</sub>:Co particles to have an elongated geometry, with lengths in the range 100-200 nm and thicknesses around 30-60 nm.

Co-doped TiO<sub>2</sub> nanopowders were used as precursors to produce Ti/Co oxide composites. Precursor TiO<sub>2</sub>:Co nanopowders were annealed at 650 °C for 8 h with synthetic air flow (FigureS5). XRD patterns of the annealed materials (Figure 1a) displayed the characteristic peaks of both anatase TiO<sub>2</sub> (JCPDS no.01-073-1764)<sup>28</sup> and CoTiO<sub>3</sub> (JCPDS 01-077-1373)<sup>29</sup>. As expected, with Co content increasing in the precursor material, the relative intensity of the CoTiO<sub>3</sub> diffraction peaks became stronger (Figure 1a). Besides, the shift of the anatase peaks detected in the precursor TiO<sub>2</sub>:Co materials disappeared, indicating the segregation of Co ions to form the CoTiO<sub>3</sub> phase. TEM analysis showed the particles within the annealed powder to just partially preserve the elongated geometry of the precursor (Figure 1c, S7). Besides, elemental maps showed the  $CoTiO_3$  phase to be evenly distributed throughout the  $CoTiO_3/TiO_2$  nanocomposite, within crystal domains of a similar size as those of  $TiO_2$  (Figure 1d).



**Figure 1**. a) XRD patterns of CoTiO<sub>3</sub>/TiO<sub>2</sub> (0, 1, 2, 5%). b,c) TEM micrograph and atomic scheme of the precursor TiO<sub>2</sub>:Co (1%) nanopowder (b) and the CoTiO<sub>3</sub>/TiO<sub>2</sub> (1%) nanocomposite (c). d) STEM image of a CoTiO<sub>3</sub>/TiO<sub>2</sub> composite and corresponding EELS elemental maps for Ti, O, Co and its combinations as noted in each map.

As reference materials, pure  $TiO_2$  and  $CoTiO_3$  powders were synthesized by decomposition of titanium (IV) isopropoxide and proper amounts of titanium (IV) isopropoxide and cobalt (II) nitrate, respectively (see details in the experimental section). XRD patterns of the annealed samples (Figure 2a) displayed the pure anatase  $TiO_2$  and  $CoTiO_3$ phases, respectively. The bandgaps of  $TiO_2$  and  $CoTiO_3$ , estimated via the Tauc plot from the UV-visible absorption spectra,<sup>30</sup> were 3.0 eV and 2.3 eV, respectively (Figure 2b, S10). TEM/HRTEM micrographs of  $TiO_2$  and  $CoTiO_3$  nanopowders showed them to be composed





**Figure 2**. a) XRD patterns of  $TiO_2$  and  $CoTiO_3$ , b) Kubelka-Munk function for  $TiO_2$  and  $CoTiO_3$  with a linear fit to determine the band gap energy.

#### Photocatalytic hydrogen production

Figure 3a,b displays the UV photocatalytic activity of CoTiO<sub>3</sub>/TiO<sub>2</sub> nanopowders with different amount of CoTiO<sub>3</sub> in the production of hydrogen from ethanol dehydration using a 10% ethanol solution in water. The activities of the reference TiO<sub>2</sub> and CoTiO<sub>3</sub> catalysts and that of the Co-doped TiO<sub>2</sub> were also measured and displayed. The hydrogen evolution rate (HER) measured under UV light ( $365 \pm 5$  nm) for the reference TiO<sub>2</sub> and CoTiO<sub>3</sub> catalysts was 1.8 and 0.3 mmol h<sup>-1</sup>·g<sup>-1</sup>, respectively. On the other hand, among the series of CoTiO<sub>3</sub>/TiO<sub>2</sub> samples tested, the CoTiO<sub>3</sub>/TiO<sub>2</sub> (1%) photocatalyst exhibited the highest HER, 3.7 mmol h<sup>-1</sup>·g<sup>-1</sup>, a twofold higher than TiO<sub>2</sub> and a factor 12 above CoTiO<sub>3</sub>. Under the same conditions, the HER of the TiO<sub>2</sub>:Co (1%) catalyst was just 0.5 mmol h<sup>-1</sup>·g<sup>-1</sup>. Actually, as shown in figure S9, all the nanocomposites CoTiO<sub>3</sub>/TiO<sub>2</sub> (0.5, 2 and 5%) displayed significantly larger HER than those obtained from Co-doped titania, TiO<sub>2</sub>:Co (0.5, 2 and 5%).

Figure 3c shows the HER photocatalytic activities under UV light  $(372 \pm 5 \text{ nm})$  when adding visible light or heat (see experimental section for details). Experiments involved four consecutive steps: 1) Upon turning on the UV light, HER began to increase until it stabilized. At this point the sample temperature was ca. 24 °C; 2) With the UV light on, the visible light was turned on, which increased the HER of most of the samples. The addition of visible light also increased the sample temperature, up to ca. 34-36 °C; 3) Maintaining the UV light on, the visible light was turned off, what resulted in a relatively slow decrease of the HER and a temperature decrease down to 24 °C. The slow HER decrease already denoted a significant effect of temperature on the observed increase of HER with the visible light; 4) Still with the UV light on, the reactor was heated to 34-36 °C, which also resulted in an increase of the HER for most catalysts. Comparing HER obtained in stages 2 and 4 (Figure 3c, d), it was observed that the addition of visible light or heat resulted in a very significant increase of HER for most samples. In the case of the reference  $TiO_2$  catalyst and the Co-doped  $TiO_2$ , the very significant activity enhancement obtained with the visible light was fully associated to the slight increase of temperature. Notice that almost a twofold increase of HER was obtained with a temperature change of just 10 °C, which opens the door for an efficient solar energy conversion though thermo-photocatalytic process. CoTiO<sub>3</sub>/TiO<sub>2</sub> catalysts also showed an important increase of activity with the minor increase of temperature tested. However, CoTiO<sub>3</sub>/TiO<sub>2</sub> samples displayed a much more significant increase of HER when incorporating the visible light irradiation than when just heating the sample to the reached temperature. Among the different CoTiO<sub>3</sub>/TiO<sub>2</sub> composites, CoTiO<sub>3</sub>/TiO<sub>2</sub> (1%) displayed the highest performance when combining UV and visible light. Finally, the incorporation of visible light or temperature had a minor influence on the HER of CoTiO<sub>3</sub>.



**Figure 3**. a) Photocatalytic H<sub>2</sub> evolution on TiO<sub>2</sub>, CoTiO<sub>3</sub>/TiO<sub>2</sub> (1, 2, 5%), TiO<sub>2</sub>:Co (1%) and CoTiO<sub>3</sub> under UV light irradiation (365  $\pm$  5 nm, 79.1  $\pm$  0.5 mW·cm<sup>-2</sup>). b) HER from data

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displayed in (a). c) HER measured from CoTiO<sub>3</sub>/TiO<sub>2</sub> (0.5, 1, 5%), TiO<sub>2</sub>, CoTiO<sub>3</sub>, TiO<sub>2</sub>:Co (1%) under different conditions: 1) UV light irradiation ( $372 \pm 5 \text{ nm}$ ,  $11.2 \pm 0.5 \text{ mW} \cdot \text{cm}^{-2}$ ); 2) UV ( $372 \pm 5 \text{ nm}$ ,  $11.2 \pm 0.5 \text{ mW} \cdot \text{cm}^{-2}$ ) plus visible light irradiation ( $0.017 \pm 0.005 \text{ mW} \cdot \text{cm}^{-2}$ ); 3) UV light irradiation, 4) UV light irradiation and heating to compensate temperature (~34-36 °C); d) HER obtained from data displayed in (c).

A comparison of the XRD patterns and TEM images of the  $CoTiO_3/TiO_2$  (5%) sample before and after the photocatalytic tests (Figures S11, S12) revealed no apparent changes, suggesting that the  $CoTiO_3/TiO_2$  heterojunction possessed a good structural photostability.

The photocatalytic performance of semiconductor materials is closely related to the charge separation, transport and transfer processes that strongly depend on their relative electronic energy level positions. To gain insights from the photocatalytic process and to understand the enhanced performance of CoTiO<sub>3</sub>/TiO<sub>2</sub> composites, a set of spectroscopic analysis was carried out. The steady-state PL spectra recorded on  $TiO_2$  and  $CoTiO_3/TiO_2$  (1%) showed a characteristic peak around 400 nm (Figure 4a), which was in line with recent reports on PL spectra of TiO<sub>2</sub>.<sup>31, 32</sup> The lower PL intensity of the CoTiO<sub>3</sub>/TiO<sub>2</sub> composite originated from the reduced radiative charge recombination in TiO<sub>2</sub> due to CoTiO<sub>3</sub> incorporation. Similar PL attenuation effects were reported by Chen et al. on noble-metal-decorated TiO<sub>2</sub> nanocrystals<sup>32</sup> and by Zuo et al. on SnS<sub>2</sub>-Pt nanoheterostructures.<sup>33</sup> To analyze the role of CoTiO<sub>3</sub>, TRPL spectra of TiO<sub>2</sub> and CoTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures were measured and compared. The TRPL spectra tracked at 400 nm is shown in Figure 4b. The PL intensity of CoTiO<sub>3</sub>/TiO<sub>2</sub> (1%) was observed to decay significantly slower than for pristine TiO<sub>2</sub>. The fitting revealed an average lifetime of 35.8 ns for CoTiO<sub>3</sub>/TiO<sub>2</sub> (1%) and 5.9 ns for TiO<sub>2</sub>. The longer lifetime recorded over CoTiO<sub>3</sub>/TiO<sub>2</sub> proved that the heterojunction contributed to the charge separation, increasing in this way their recombination time.



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**Figure 4.** a) Steady-state photoluminescence spectra. b) Time-resolved photoluminescence spectra with corresponding fitting curves.

TPC and EIS measurements were conducted using photocatalysts films deposited on FTO substrates (see experimental section for details). As shown in Figure 5a, the loading of CoTiO<sub>3</sub> on TiO<sub>2</sub> resulted in enhanced photocurrent responses, with a higher steady-state photocurrent at 0.6 V vs RHE that may be related to an improved charge transfer process. Notably, TPC spikes, whose amplitude represents the degree of surface recombination,<sup>34</sup> were larger in pristine TiO<sub>2</sub> than in CoTiO<sub>3</sub>/TiO<sub>2</sub> (1%). This result indicated that the CoTiO<sub>3</sub>/TiO<sub>2</sub> heterojunction efficiently suppresses the surface charge recombination process. Similar TPC response have been reported on other photocatalyst systems, for example, carbon nanotube loaded TiO<sub>2</sub>,<sup>35</sup> TiO<sub>2</sub>/Fe<sub>2</sub>TiO<sub>5</sub>/Fe<sub>2</sub>O<sub>3</sub> triple-heterojunction,<sup>36</sup> and Bi<sub>2</sub>O<sub>3</sub>@TiO<sub>2</sub> photocatalyst.<sup>37</sup>

EIS measurements showed that qualitatively speaking, and as deduced from the Nyquist plots (Figure 5b), CoTiO<sub>3</sub>/TiO<sub>2</sub> (1%) was less resistive than TiO<sub>2</sub>,<sup>38</sup> indicating that the formation of the heterojunction facilitated the charge transport process. As shown in the inset of Figure 5b, a Randles equivalent circuit was employed to fit the data, which consisted of a series resistor  $R_s$ , a bulk resistor  $R_{ct,bulk}$  for charge transport resistance, and a bulk capacitor  $C_{bulk}$  for space charge region capacitance.<sup>39</sup> The data fitting showed that CoTiO<sub>3</sub>/TiO<sub>2</sub> (1%) had two times lower  $R_{ct,bulk}$  than TiO<sub>2</sub>. With only 1% incorporation of CoTiO<sub>3</sub> on TiO<sub>2</sub> the value of  $R_{ct,bulk}$  was reduced a twofold, from 5.77 k $\Omega$  to 2.68 k $\Omega$ . Likewise, the electron lifetime,  $\tau_n$ , could be estimated by the RC time constant of the Randles circuit.<sup>30</sup> Generally speaking,  $\tau_n$  characterizes the electron recombination; a shorter  $\tau_n$  means a faster recombination process. The formation of the CoTiO<sub>3</sub>/TiO<sub>2</sub> heterojunction boosted  $\tau_n$  from 1.3 ms to 2.9 ms, which implies that the heterojunction reduced charge recombination probably due to a promoted charge separation, consistent with TRPL results.



 **Figure 5.** a) Transient photocurrent response. b) Nyquist plot of impedance response with corresponding equivalent circuit for fitting.

#### Photocatalytic Mechanism

Using UPS, the valence band maximum (VBM) of the TiO<sub>2</sub> and CoTiO<sub>3</sub> reference materials was determined to be at -6.57 eV and -7.13 eV vs vacuum, respectively (Figure 6a).<sup>15, 40,41</sup> Taking into account the measured band gaps and VBM position, the band alignment between TiO<sub>2</sub> and CoTiO<sub>3</sub> corresponded to that of a type II heterostructure (left scheme in Figure 7). Thus, considering a type-II heterojunction charge-transfer mechanism, within the CoTiO<sub>3</sub>/TiO<sub>2</sub> heterojunction photogenerated electrons would travel from TiO<sub>2</sub> to CoTiO<sub>3</sub>, and holes from CoTiO<sub>3</sub> to TiO<sub>2</sub>. However, because the conduction band maximum (CBM) of CoTiO<sub>3</sub> is at lower position than the H<sub>2</sub>/H<sup>+</sup> level, the free electrons of CoTiO<sub>3</sub> see an energy barrier to reduce H<sup>+</sup> into H<sub>2</sub> (left scheme in Figure 7).<sup>41</sup> This does not match well with the enhanced photocatalytic performance observed in CoTiO<sub>3</sub>/TiO<sub>2</sub> composites with respect to TiO<sub>2</sub>.

Actually, taking into account the electron energy band position of the two materials and intrinsic n-type character of TiO<sub>2</sub> and p-type character of CoTiO<sub>3</sub>, upon placing the two materials in contact an injection of electrons from the TiO<sub>2</sub> to the CoTiO<sub>3</sub> will occur. This charge redistribution will create an electric field at the interphase. In view of the small size of the crystallites and the moderate charge carrier concentration characterizing these type of materials, this electric field will probably extend through the whole  $TiO_2$  and  $CoTiO_3$  domains. The electric field will thus drive electrons photogenerated within the TiO<sub>2</sub> and holes photogenerated within CoTiO<sub>3</sub> away from the interphase, and holes photogenerated within the  $TiO_2$  and electrons photogenerated within the CoTiO\_3 towards the interphase, where they probably recombine (right scheme in Figure 7). As a result, photogenerated electrons in the conduction band of  $TiO_2$ , thus having a high reduction potential, are driven toward the surface with a reduced probability of recombination with valence band holes. Thus  $TiO_2$ photogenerated electrons could reduce protons into hydrogen more effectively. Likewise, photogenerated holes in the valence band of CoTiO<sub>3</sub>, i.e. with a strong oxidation potential, are driven to the surface with a lower chance to recombine with conduction band electrons. Thus, CoTiO<sub>3</sub> photogenerated holes can more efficiently drive ethanol dehydrogenation to acetaldehyde and protons. Overall, a clear synergism between the two materials is stablished through this direct Z-scheme charge transfer mechanism.<sup>42-46</sup>



**Figure 6.** a) UPS spectrum for  $TiO_2$  and  $CoTiO_3$ . b) O 1s XPS spectra of  $TiO_2$ ,  $CoTiO_3$ ,  $CoTiO_3/TiO_2$  (0.5%) and  $CoTiO_3/TiO_2$  (1%).

Finally, figures 6b and S8 show the O1s, Ti 2p and Co 2p XPS spectra of the reference samples and two CoTiO<sub>3</sub>/TiO<sub>2</sub> composites. The most interesting aspect of these analyses was the additional peak (532.5 eV) appearing at lower binding energy than the main O 1s peak (529.6 eV) corresponding to lattice oxygen. This new peak should be associated with  $OH^-$  groups.<sup>47</sup> The notable increase of surface adsorbed species and particularly hydroxyl groups in the CoTiO<sub>3</sub>/TiO<sub>2</sub> composites is indicative of the promoted charge separation and tendency of part of the charge carriers to migrate toward the surface, away from an interphase, where they can promote molecular adsorption and redox reactions.



**Figure 7.** Schematic illustration of the relative energy levels of  $TiO_2$  and  $CoTiO_3$  and simplified charge transfer mechanism between  $TiO_2$  and  $CoTiO_3$  in a conventional type II heterostructure and a direct Z-scheme.

# CONCLUSION

A simple method for the synthesis of CoTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures with tuned CoTiO<sub>3</sub> amounts was presented. The materials showed an excellent activity in the photocatalytic hydrogen evolution from ethanol dehydrogenation, with HER under UV light well above those of TiO<sub>2</sub>, CoTiO<sub>3</sub> and Co-doped TiO<sub>2</sub>. We also observed a significant influence of visible light on the HER of CoTiO<sub>3</sub>/TiO<sub>2</sub> heterostructures beyond the important effect of the increased temperature. Electrochemical impedance spectroscopy and static and time resolved PL measurements showed the formed heterostructures to promote charge separation, extending the life time of photogenerated charge carriers. UV-vis spectroscopy and UPS analysis showed the alignment of the energy levels of the two materials to resemble a type II heterostructure, with the CBM of the CoTiO<sub>3</sub> below the  $H_2/H^+$  energy level. In such type II heterostructures electron transfer from n-type  $TiO_2$  to p-type CoTiO<sub>3</sub> is to be expected, generating an electric field within the material that drives photogenerated electrons within TiO<sub>2</sub> and photogenerated holes within CoTiO<sub>3</sub> away from the interphase and photogenerated holes in TiO<sub>2</sub> and electrons in CoTiO<sub>3</sub> towards the interphase where they recombine. All these evidences pointed out toward a direct Z-scheme mechanism as responsible of the enhanced photocatalytic ethanol dehydrogenation activity of CoTiO<sub>3</sub>/TiO<sub>2</sub> composites over that of TiO<sub>2</sub>.

### **EXPERIMENTAL SECTION**

*Chemicals*: Titanium (IV) isopropoxide (97%), hexadecylamine (HDA, 90%) and ammonium hydroxide (28-30%) were ordered from Sigma Aldrich. Ethanol (96%) was purchased from PanReac AppliChem ITW Reagents. Cobalt (II) nitrate hexahydrate (98%) was purchased from Fluka.

Synthesis of Photocatalysts ( $TiO_2$ ,  $CoTiO_3$  and  $CoTiO_3/TiO_2$ ): First, 0.45 g HDA was mixed with 40 mL ethanol at room temperature and stirred for 5 mins. Then, an accurate quantity of  $Co(NO_3)_2 \cdot 6H_2O$  (0, 11.3, 22.5, 45, 112.5 and 1.2 g to get 0, 0.5, 1, 2, 5 and 100 mol% concentrations, respectively) was introduced under stirring for another 5 min. At this point, 2.3 mL titanium isopropoxide was added dropwise and kept stirring 16 h at ambient temperature. The mixture was washed 3 times with ethanol by centrifuging to collect the final product. The product was subsequently mixed with a solution including 20 mL of ethanol, 10 mL of MiliQ water and 2.2 mL of ammonium hydroxide, kept for 16 h without stirring. The mixture was then placed in an autoclave reactor with a Teflon liner (50 mL) and maintained at 170 °C for

14 h. TiO<sub>2</sub> and CoTiO<sub>3</sub> were obtained by annealing dried samples at 650  $^{\circ}$ C for 8 h with synthetic air flow.

*Characterization*: The particle morphology and size were analyzed using transmission electron microscopy (TEM) in a ZEISS LIBRA 120, working at 120 KeV. High angle annular dark field (HAADF) scanning TEM and high-resolution TEM (HRTEM) analysis were performed on a FEI Tecnai F20 field emission gun microscope operated at 200 keV combined with a Gatan Quantum electron energy-loss spectroscopy (EELS) detector. Scanning electron microscopy (SEM) was conducted using a ZEISS Auriga microscope. X-ray diffraction analyses (XRD) were carried out on a Bruker D8-Advance X-ray diffractometer (20: 20°-80°, scanning rate was set to 5°/min). The optical properties of photocatalysts were evaluated by UV/Visible diffuse spectroscopy (UV-Vis-NIR Shimadzu 3600). X-ray photoelectron spectroscopy (XPS) was conducted with an Al anode XR50 source on a SPECS equipment using a Phoibos 150 MCD-9 detector (150 W). Steady-state photoluminescence (PL) spectra were conducted by a highresolution photoluminescence spectrofluorometer (Horiba Jobin Yvon Fluorolog-3). For the time-resolved photoluminescence spectroscopy (TRPL) measurements, a nanosecond LED with 350 nm peak wavelength (Horiba NanoLED N-390, pulse width < 1.3 ns) was applied to excite the samples. TRPL decay was resolved at 400 nm. Average lifetimes were obtained by fitting the TPPL spectra with DAS6 software (Horiba). Transient photocurrent (TPC) and electrochemical impedance spectroscopy (EIS) analyses were conducted using a Bio-Logic SP-300. Photocatalysts were coated on transparent conducting substrates (FTO) and were used as working electrode. Ag/AgCl was used as reference electrode and a Pt wire as counter electrode. For impedance characterization, a sinusoidal potential was applied to the working electrode with an amplitude of 25 mV and a frequency in the range 100 kHz - 50 mHz. Impedance response fitting was conducted using ZView (Scribner Associates). In TPC measurements, the same three-electrode configuration was employed and a Xenon arc lamp (Newport, 450 W) was used as light source. UV photoelectron Spectroscopy (UPS) measurements were performed on a Thermo Fisher Scientific Escalab 250Xi.

*Photocatalytic Hydrogen Evolution Measurements*: A cellulose paper impregnated with the photocatalyst (2.0 mg) was holded inside a photocatalytic reactor equipped with  $365 \pm 5$  nm UV LEDs (Figure S1). Light irradiation at the sample position was was 79.1 mW·cm<sup>-2</sup>. Saturated Ar gas stream was prepared by bubbling Ar (20 mL·min<sup>-1</sup>) through a Dreschel bottle containing a water-ethanol vapour mixture with a molar ratio 9. The photoreactor exit was analysed online by gas chromatography equipped with Plot U, MS 5 Å, and Stabilwax columns

every 4 min. Saturated Ar was purged into system (20 mL·min<sup>-1</sup>, 30 min) to remove oxygen before performing the experiment. The UV-visible light source contained two LEDs emitting at 372  $\pm$  5 nm and two LEDs emitting visible light (correlated color temperature 6099 K, color rendering index 74) Figure S1. In this system light irradiation at the sample position was 11.2  $\pm$  0.5 mW·cm<sup>-2</sup> for UV light and 0.017  $\pm$  0.005 mW·cm<sup>-2</sup> for visible light.<sup>48-50</sup>

# **ASSOCIATED CONTENT**

Supporting Information. Supporting information contains photocatalytic reactor, additional TEM and HRTEM characterization, XPS analysis, Elemental composition analysis, Photocatalytic H2 production rates and UV-vis analysis.

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# C. Xing and Y. Liu contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

# NOTES

The authors declare no competing financial interest.

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