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Complete List of Authors:	Xing, Congcong; Institut de Recerca en Energia de Catalunya (IREC), Liu, Yongpeng; Ecole Polytechnique Federale de Lausanne, Institute of Chemical Sciences and Engineering Zhang, Yu; Institut de Recerca en Energia de Catalunya, Wang, Xiang; Universitat de Barcelona, Institut de Recerca en Energia de Catalunya (IREC) Guardia, Pablo; IREC Yao, Liang; Ecole Polytechnique Federale de Lausanne, Han, Xu; ICN2 Zhang, Ting; ICN2 Arbiol, Jordi; ICREA and Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology (BIST), Advanced Electron Nanoscopy Soler, Lluís ; Universitat Politècnica de Catalunya, Institute of Energy Technologies Chen, Yufen; Universitat Politècnica de Catalunya Sivula, Kevin; Ecole Polytechnique Federale de Lausanne, EPFL SB ISIC LIMNO Guijarro, Nestor; École Polytechnique Fédérale de Lausanne Cabot, Andreu; Catalonia Institute for Energy Research, Dept Electrònica Llorca, Jordi; Universitat Politècnica de Catalunya, Institute of Energy Technologies

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A direct Z-scheme for the photocatalytic hydrogen production from ethanol dehydrogenation on CoTiO₃/TiO₂ heterostructures

Congcong Xing,^{a,b,†} Yongpeng Liu,^{c,†} Yu Zhang,^a Xiang Wang,^a Pablo Guardia,^a Liang Yao,^c Xu Han,^d Ting Zhang,^d Jordi Arbiol,^{d,e} Lluís Soler,^b Yufen Chen,^b Kevin Sivula,^c Néstor Guijarro,^c Andreu Cabot,^{*a,e} Jordi Llorca ^{*b}

^a Catalonia Institute for Energy Research (IREC), Sant Adrià de Besòs, 08930 Barcelona, Spain

^b Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, EEBE, 08019 Barcelona, Spain

^c Laboratory for Molecular Engineering of Optoelectronic Nanomaterials (LIMNO), École Polytechnique Fédérale de Lausanne (EPFL), Station 6, CH-1015 Lausanne, Switzerland

^d Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Catalonia, Spain

^e ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain

[†]These authors contributed equally to this work.

* E-mails: A. Cabot: acabot@irec.cat; J. Llorca: jordi.llibre@upc.edu.

ABSTRACT

Photocatalytic H₂ evolution from ethanol dehydrogenation is a convenient strategy to store solar energy in a highly valuable fuel with potential zero net CO₂ balance. Herein, we report on the synthesis of CoTiO₃/TiO₂ composite catalysts with controlled amounts of highly distributed CoTiO₃ 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 CoTiO₃/TiO₂ heterostructures to have a type II band alignment, with the conduction band minimum of CoTiO₃ below the H₂/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 CoTiO₃/TiO₂ 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

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, H₂ 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 CO₂ 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 (~10¹¹ 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.¹⁻⁴ Ethanol biosourcing compensates the CO₂ released during combustion through its capture during photosynthesis, leading to a near zero net CO₂ footprint. Besides, being liquid at ambient temperature, ethanol can be easily stored and transported, to the point that the already established infrastructure for ethanol production and distribution makes it a very convenient precursor of other fuels, including H₂ and higher alcohols.^{4, 5}

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.^{6, 7}

Photocatalysts allow the production of molecular hydrogen from ethanol dehydrogenation using solar energy as unique energy input.¹ In the simplest scenario, ethanol can be photocatalytically dehydrogenated at ambient pressure and temperature, yielding molecular hydrogen and acetaldehyde, and releasing no CO₂:

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.⁸⁻

¹⁰ 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.^{4, 11, 12}

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.⁷ 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_2) is the prototype photocatalyst due to its outstanding optoelectronic properties, natural abundance, high photocorrosion resilience, lack of toxicity and low cost.^{13, 14} However, TiO_2 practical application is hampered by its large bandgap, that limits the range of solar spectra used.^{15, 16} 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_3) is a narrow band gap oxide semiconductor with a ABO_3 perovskite crystal structure, large carrier mobility, excellent stability, and high absorption coefficient.¹⁷⁻¹⁹ In combination with graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) and Pt, it has been recently explored for photocatalytic hydrogen generation through a direct Z-scheme, where holes photogenerated in CoTiO_3 participate in the oxidation reaction, electrons photogenerated in the $\text{g-C}_3\text{N}_4$ drive the reduction reaction, and at the interphase of the two materials electrons photogenerated in CoTiO_3 recombine with holes generated in $\text{g-C}_3\text{N}_4$.¹⁷ $\text{CoTiO}_3/\text{TiO}_2$ composites have also been synthesized and used in multiple applications, including photoelectrochemical water splitting;²⁰ photocatalytic dye degradation,²¹ oxidative dehydrogenation of cyclohexane;²² dry reforming of methane;²³ peroxymonosulfate activation

and metronidazole degradation;²⁴ resistive humidity sensing;²⁵ electrochemical sensing of dopamine;²⁶ and anode in lithium ion batteries,²⁷ but surprisingly CoTiO₃/TiO₂ composites have not been thoroughly tested as photocatalysts for H₂ production from bioethanol dehydrogenation.

Herein, CoTiO₃/TiO₂ photocatalysts with different CoTiO₃ amounts are produced by phase segregation during annealing of a Co-doped TiO₂ precursor prepared by hydrothermal reaction. CoTiO₃/TiO₂ 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.^{2, 3, 5}

RESULTS AND DISCUSSION

Photocatalysts Characterization

Cobalt-doped titania (TiO₂: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 TiO₂ 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 TiO₂ lattice structure. EDX, XPS, ICP analysis showed the TiO₂: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 TiO₂:Co particles to have an elongated geometry, with lengths in the range 100-200 nm and thicknesses around 30-60 nm.

Co-doped TiO₂ nanopowders were used as precursors to produce Ti/Co oxide composites. Precursor TiO₂: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 TiO₂ (JCPDS no.01-073-1764)²⁸ and CoTiO₃ (JCPDS 01-077-1373)²⁹. As expected, with Co content increasing in the precursor material, the relative intensity of the CoTiO₃ diffraction peaks became stronger (Figure 1a). Besides, the shift of the anatase peaks detected in the precursor TiO₂:Co materials disappeared, indicating the segregation of Co ions to form the CoTiO₃ 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 $\text{CoTiO}_3/\text{TiO}_2$ nanocomposite, within crystal domains of a similar size as those of TiO_2 (Figure 1d).

Figure 1. a) XRD patterns of $\text{CoTiO}_3/\text{TiO}_2$ (0, 1, 2, 5%). b,c) TEM micrograph and atomic scheme of the precursor $\text{TiO}_2:\text{Co}$ (1%) nanopowder (b) and the $\text{CoTiO}_3/\text{TiO}_2$ (1%) nanocomposite (c). d) STEM image of a $\text{CoTiO}_3/\text{TiO}_2$ 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,³⁰ 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

of irregular shaped particle with an average size of ca. 30 and 60 nm, respectively (Figures S3, S4).

Figure 2. a) XRD patterns of TiO₂ and CoTiO₃, b) Kubelka-Munk function for TiO₂ and CoTiO₃ with a linear fit to determine the band gap energy.

Photocatalytic hydrogen production

Figure 3a,b displays the UV photocatalytic activity of CoTiO₃/TiO₂ nanopowders with different amount of CoTiO₃ in the production of hydrogen from ethanol dehydration using a 10% ethanol solution in water. The activities of the reference TiO₂ and CoTiO₃ catalysts and that of the Co-doped TiO₂ were also measured and displayed. The hydrogen evolution rate (HER) measured under UV light (365 ± 5 nm) for the reference TiO₂ and CoTiO₃ catalysts was 1.8 and 0.3 mmol h⁻¹·g⁻¹, respectively. On the other hand, among the series of CoTiO₃/TiO₂ samples tested, the CoTiO₃/TiO₂ (1%) photocatalyst exhibited the highest HER, 3.7 mmol h⁻¹·g⁻¹, a twofold higher than TiO₂ and a factor 12 above CoTiO₃. Under the same conditions, the HER of the TiO₂:Co (1%) catalyst was just 0.5 mmol h⁻¹·g⁻¹. Actually, as shown in figure S9, all the nanocomposites CoTiO₃/TiO₂ (0.5, 2 and 5%) displayed significantly larger HER than those obtained from Co-doped titania, TiO₂:Co (0.5, 2 and 5%).

Figure 3c shows the HER photocatalytic activities under UV light (372 ± 5 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 TiO₂ catalyst and the Co-doped TiO₂, 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 through thermo-photocatalytic process. CoTiO₃/TiO₂ catalysts also showed an important increase of activity with the minor increase of temperature tested. However, CoTiO₃/TiO₂ 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 CoTiO₃/TiO₂ composites, CoTiO₃/TiO₂ (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 CoTiO₃.

Figure 3. a) Photocatalytic H₂ evolution on TiO₂, CoTiO₃/TiO₂ (1, 2, 5%), TiO₂:Co (1%) and CoTiO₃ under UV light irradiation (365 ± 5 nm, 79.1 ± 0.5 mW·cm⁻²). b) HER from data

displayed in (a). c) HER measured from CoTiO₃/TiO₂ (0.5, 1, 5%), TiO₂, CoTiO₃, TiO₂:Co (1%) under different conditions: 1) UV light irradiation (372 ± 5 nm, 11.2 ± 0.5 mW·cm⁻²); 2) UV (372 ± 5 nm, 11.2 ± 0.5 mW·cm⁻²) plus visible light irradiation (0.017 ± 0.005 mW·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 CoTiO₃/TiO₂ (5%) sample before and after the photocatalytic tests (Figures S11, S12) revealed no apparent changes, suggesting that the CoTiO₃/TiO₂ 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 CoTiO₃/TiO₂ composites, a set of spectroscopic analysis was carried out. The steady-state PL spectra recorded on TiO₂ and CoTiO₃/TiO₂ (1%) showed a characteristic peak around 400 nm (Figure 4a), which was in line with recent reports on PL spectra of TiO₂.^{31, 32} The lower PL intensity of the CoTiO₃/TiO₂ composite originated from the reduced radiative charge recombination in TiO₂ due to CoTiO₃ incorporation. Similar PL attenuation effects were reported by Chen et al. on noble-metal-decorated TiO₂ nanocrystals³² and by Zuo et al. on SnS₂-Pt nanoheterostructures.³³ To analyze the role of CoTiO₃, TRPL spectra of TiO₂ and CoTiO₃/TiO₂ heterostructures were measured and compared. The TRPL spectra tracked at 400 nm is shown in Figure 4b. The PL intensity of CoTiO₃/TiO₂ (1%) was observed to decay significantly slower than for pristine TiO₂. The fitting revealed an average lifetime of 35.8 ns for CoTiO₃/TiO₂ (1%) and 5.9 ns for TiO₂. The longer lifetime recorded over CoTiO₃/TiO₂ proved that the heterojunction contributed to the charge separation, increasing in this way their recombination time.

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_3 on TiO_2 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,³⁴ were larger in pristine TiO_2 than in $\text{CoTiO}_3/\text{TiO}_2$ (1%). This result indicated that the $\text{CoTiO}_3/\text{TiO}_2$ heterojunction efficiently suppresses the surface charge recombination process. Similar TPC response have been reported on other photocatalyst systems, for example, carbon nanotube loaded TiO_2 ,³⁵ $\text{TiO}_2/\text{Fe}_2\text{TiO}_5/\text{Fe}_2\text{O}_3$ triple-heterojunction,³⁶ and $\text{Bi}_2\text{O}_3@\text{TiO}_2$ photocatalyst.³⁷

EIS measurements showed that qualitatively speaking, and as deduced from the Nyquist plots (Figure 5b), $\text{CoTiO}_3/\text{TiO}_2$ (1%) was less resistive than TiO_2 ,³⁸ 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.³⁹ The data fitting showed that $\text{CoTiO}_3/\text{TiO}_2$ (1%) had two times lower $R_{ct,bulk}$ than TiO_2 . With only 1% incorporation of CoTiO_3 on TiO_2 the value of $R_{ct,bulk}$ was reduced a twofold, from 5.77 $\text{k}\Omega$ to 2.68 $\text{k}\Omega$. Likewise, the electron lifetime, τ_n , could be estimated by the RC time constant of the Randles circuit.³⁰ Generally speaking, τ_n characterizes the electron recombination; a shorter τ_n means a faster recombination process. The formation of the $\text{CoTiO}_3/\text{TiO}_2$ heterojunction boosted τ_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_2 and CoTiO_3 reference materials was determined to be at -6.57 eV and -7.13 eV vs vacuum, respectively (Figure 6a).^{15, 40, 41} Taking into account the measured band gaps and VBM position, the band alignment between TiO_2 and CoTiO_3 corresponded to that of a type II heterostructure (left scheme in Figure 7). Thus, considering a type-II heterojunction charge-transfer mechanism, within the $\text{CoTiO}_3/\text{TiO}_2$ heterojunction photogenerated electrons would travel from TiO_2 to CoTiO_3 , and holes from CoTiO_3 to TiO_2 . However, because the conduction band maximum (CBM) of CoTiO_3 is at lower position than the H_2/H^+ level, the free electrons of CoTiO_3 see an energy barrier to reduce H^+ into H_2 (left scheme in Figure 7).⁴¹ This does not match well with the enhanced photocatalytic performance observed in $\text{CoTiO}_3/\text{TiO}_2$ composites with respect to TiO_2 .

Actually, taking into account the electron energy band position of the two materials and intrinsic n-type character of TiO_2 and p-type character of CoTiO_3 , upon placing the two materials in contact an injection of electrons from the TiO_2 to the CoTiO_3 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_2 and holes photogenerated within CoTiO_3 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_3 , i.e. with a strong oxidation potential, are driven to the surface with a lower chance to recombine with conduction band electrons. Thus, CoTiO_3 photogenerated holes can more efficiently drive ethanol dehydrogenation to acetaldehyde and protons. Overall, a clear synergism between the two materials is established through this direct Z-scheme charge transfer mechanism.⁴²⁻⁴⁶

Figure 6. a) UPS spectrum for TiO₂ and CoTiO₃. b) O 1s XPS spectra of TiO₂, CoTiO₃, CoTiO₃/TiO₂ (0.5%) and CoTiO₃/TiO₂ (1%).

Finally, figures 6b and S8 show the O1s, Ti 2p and Co 2p XPS spectra of the reference samples and two CoTiO₃/TiO₂ 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.⁴⁷ The notable increase of surface adsorbed species and particularly hydroxyl groups in the CoTiO₃/TiO₂ 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 TiO₂ and CoTiO₃ and simplified charge transfer mechanism between TiO₂ and CoTiO₃ in a conventional type II heterostructure and a direct Z-scheme.

CONCLUSION

A simple method for the synthesis of $\text{CoTiO}_3/\text{TiO}_2$ heterostructures with tuned CoTiO_3 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_2 , CoTiO_3 and Co-doped TiO_2 . We also observed a significant influence of visible light on the HER of $\text{CoTiO}_3/\text{TiO}_2$ 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_3 below the H_2/H^+ energy level. In such type II heterostructures electron transfer from n-type TiO_2 to p-type CoTiO_3 is to be expected, generating an electric field within the material that drives photogenerated electrons within TiO_2 and photogenerated holes within CoTiO_3 away from the interphase and photogenerated holes in TiO_2 and electrons in CoTiO_3 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 $\text{CoTiO}_3/\text{TiO}_2$ composites over that of TiO_2 .

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 $\text{CoTiO}_3/\text{TiO}_2$): First, 0.45 g HDA was mixed with 40 mL ethanol at room temperature and stirred for 5 mins. Then, an accurate quantity of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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 MilliQ 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_2 and CoTiO_3 were obtained by annealing dried samples at 650 °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 (2θ : 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 high-resolution 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 ± 5 nm UV LEDs (Figure S1). Light irradiation at the sample position was was $79.1 \text{ mW}\cdot\text{cm}^{-2}$. Saturated Ar gas stream was prepared by bubbling Ar ($20 \text{ mL}\cdot\text{min}^{-1}$) 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 ($20 \text{ mL}\cdot\text{min}^{-1}$, 30 min) to remove oxygen before performing the experiment. The UV-visible light source contained two LEDs emitting at $372 \pm 5 \text{ nm}$ 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 $11.2 \pm 0.5 \text{ mW}\cdot\text{cm}^{-2}$ for UV light and $0.017 \pm 0.005 \text{ mW}\cdot\text{cm}^{-2}$ for visible light.⁴⁸⁻⁵⁰

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.

AUTHOR INFORMATION

Corresponding Authors

* A. Cabot: acabot@irec.cat

* J. Llorca: jordi.llibre@upc.edu

ORCID

Congcong Xing: 0000-0001-7674-6720

Yongpeng Liu: 0000-0002-4544-4217

Yu Zhang: 0000-0002-0332-0013

Pablo Guardia: 0000-0001-9076-4642

Jordi Arbiol: 0000-0002-0695-1726

Lluís Soler: 0000-0003-1591-3366

Kevin Sivula: 0000-0002-8458-0270

Néstor Guijarro: 0000-0002-3277-8816

Andreu Cabot: 0000-0002-7533-3251

Jordi Llorca: 0000-0002-7447-9582

AUTHOR CONTRIBUTIONS

# 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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Graphical abstract