

## Research Article

# Synergy of the Combination of Titanate Nanotubes with Titania Nanoparticles for the Photocatalytic Hydrogen Generation from Water-Methanol Mixture Using Simulated Sunlight

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Alkali digestion of titanium nanoparticles leads, after neutralization, to the formation of titanate nanotubes with long aspect ratio. One salient change in the formation of titanate nanotubes is the observation of an extended visible absorption band up to 550 nm, responsible for their brown colour. Combination of titanate nanotubes with commercial titanium dioxide nanoparticles, either Evonik P25 or Millennium PC500, results in an enhanced photocatalytic activity for hydrogen generation from water-methanol mixtures. This synergy between the two titanium semiconductors has an optimum for a certain proportion of the two components and is observed in both the absence and the presence of platinum or gold nanoparticles. The best efficiency under simulated sunlight irradiation was for a combination of 12 wt.% titanate nanotubes containing 0.32 wt.% platinum in 88 wt.% Millennium PC500, where a two-time increase in the hydrogen generation is observed versus the activity of Millennium PC500 containing platinum. This synergy is proposed to derive from the interfacial electron transfer from titanate nanotubes undergoing photoexcitation at wavelengths in which Millennium PC500 does not absorb this form of titania nanoparticles. Our results illustrate how the combination of several titanium semiconductors can result in an enhancement efficiency with respect to their individual components.

## 1. Introduction

Photocatalysis applied to solar fuel production is a topic of much current interest and a long-term alternative to fossil fuels [1–5]. Considering the current low efficiency of the photocatalytic activity in solar fuel production enhancement of the efficiency is a continuous task. A strategy to improve the efficiency of a photocatalytic system is to combine two semiconductors in intimate contact in such a way that photoexcitation of one of the components can lead to heterojunction electron transfer between the two components [6–9]. The case that has been more extensively studied corresponds to the use of two different semiconductors such as quantum dots supported on titanium dioxide or transition metal oxide, including RuO<sub>2</sub> and WO<sub>3</sub>, on titania [10]. While the titanium dioxide in the anatase phase or the commercial Evonik P25 having a proportion of about 20%/80% rutile/anatase

is the most widely used photocatalyst, the possibility of enhancing the photocatalytic activity of this material by adding a second different form of titanium dioxide remains to be explored. In the present paper, we will show the synergy in the photocatalytic activity derived from combining TiO<sub>2</sub> nanoparticles with titanate nanotubes. The present case is also another example of optimization of the photocatalytic activity of TiO<sub>2</sub>, in this case, by adding a different form of titanium oxide.

This synergy between titanate nanotubes and titania nanoparticles has been observed for two different types of commercial titanium dioxide nanoparticles, both in the absence and in the presence of platinum or gold as cocatalyst. The interest of this research is to show the possibility that the combination of various forms of titanium-containing materials offers to optimize the photocatalytic efficiency. This synergy seems to arise from the interfacial charge transfer

between the two titanium semiconductors. We have demonstrated the applicability of this strategy based on exclusive use of titanium-containing materials for the hydrogen generation from water-methanol mixtures using simulated solar light, that is, a process of large interest in the context of conversion of sunlight into chemical energy [11–17].

## 2. Materials and Methods

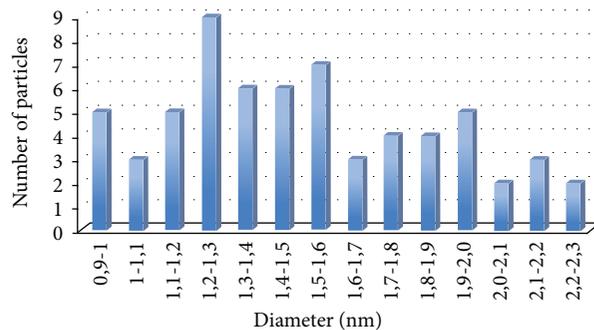
**2.1. Sample Preparation.** The  $\text{TiO}_2$  precursor used for nanotube production was a commercial  $\text{TiO}_2$  powder (Millennium PC500, anatase) consisting of pure anatase phase.  $\text{TiO}_2$  powder (3.6 g) was treated with 90 mL of aqueous 10 M NaOH solution in a Teflon-lined autoclave (total volume 200 mL) at  $125^\circ\text{C}$  for 4 days. After the hydrothermal treatment, the solid was collected by filtration and washed by suspending the solid with 2 L HCl solution ( $\text{pH} = 1.3$ ) and finally was washed with water until neutral pH. The material was dried at  $110^\circ\text{C}$  for 1 day. The deposition of gold or platinum nanoparticles was carried out by deposition-precipitation method. 0.5 g of titanate nanotubes was added to an aqueous solution containing the amount of chloroplatinic or chloroauric acid corresponding to 0.5 wt.% of metal loading. The pH was equilibrated to pH 10 by adding an aqueous solution of sodium hydroxide 0.2 M. The solid was washed with MilliQ water and dried in vacuum at ambient temperature. The metal was reduced using a  $\text{H}_2$  flow (100 mL/min) at  $300^\circ\text{C}$  for 5 h.

The preparation of mixed materials was carried out by mixing an amount of nanotubes (50 mg) with the amount of titania needed to reach a composition of 6%, 12%, 25%, and 50% in weight of nanotubes. The powders were suspended in water and the suspensions were sonicated (150 W) for 30 min to improve the homogeneity of the suspension and then were maintained under magnetic stirring overnight. The suspension was finally filtered and dried at  $110^\circ\text{C}$ .

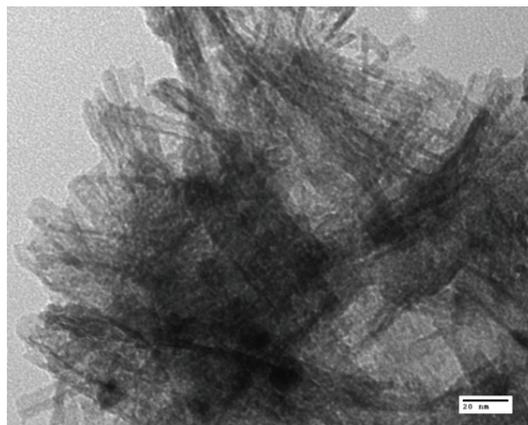
**2.2. Photocatalytic Tests for Hydrogen Production.** A suspension of the catalyst (25 mL,  $1\text{ g} \times \text{L}^{-1}$ ) was sonicated for 10 min and placed in a gas-tight reactor with an irradiation window of  $12.56\text{ cm}^2$  provided with temperature and pressure controllers. The reactor was placed in a thermostatic bath with a set point temperature of  $25^\circ\text{C}$ . The suspension was purged with an argon flow of 2 psi for 15 minutes prior to irradiation. The photoreaction was performed from the top of the photoreactor by using a solar simulator (Thermo Oriel 1000 W) with an irradiation spot of  $100\text{ cm}^2$  placed at distance of 10 cm. The light of the solar simulator was filtered through an Air Mass 1.5 filter and contained approximately 5% of UV irradiation. The amount of hydrogen collected in the headspace of the reactor was analysed by injecting  $100\ \mu\text{L}$  in a gas chromatograph using a MOLSieve column, argon as carrier gas, and a TC detector.

## 3. Result and Discussion

It had been reported that digestion of  $\text{TiO}_2$  nanoparticles in strong alkali condition leads to the formation of titanates appearing with morphology of nanotubes with long aspect



(a)



(b)

FIGURE 1: Diameter distribution and TEM image of the titanate nanotubes obtained in the present work.

ratio [18]. The average length dimension is several hundred nanometers, with diameters lower than 10 nm. We have been able to reproduce this remarkable morphological change from nanoparticles to nanotubes. Figure 1 shows representative TEM images of the resulting titanate nanotubes.

This change in morphology is accompanied by a change in the X-ray diffraction pattern, indicating that NaOH digestion has produced a phase transition from anatase to structure as presented in Figure 2.

As shown in Figure 3, a remarkable feature of these titanate nanotubes, besides the long aspect ratio, is the appearance of a residual optical absorption spanning into the visible region with a decreasing absorptivity towards long wavelengths.

This optical absorption had not been mentioned in the original report of the preparation of these materials [18]. By analogy with the reported black color for some titanium dioxide [19], we propose similarly that the brown colour of titanate nanotubes is due to the formation of a thin amorphous layer on the titanate nanotubes on top of the crystalline layers. This proposal is parallel to that recently suggested to rationalize the black colour in crystalline titanium dioxide samples obtained by submitting small titanium dioxide nanoparticles to thermal treatment at  $500^\circ\text{C}$  under hydrogen atmosphere [19]. In the present study, we have shown that these titanate nanotubes with optical absorption in the visible region

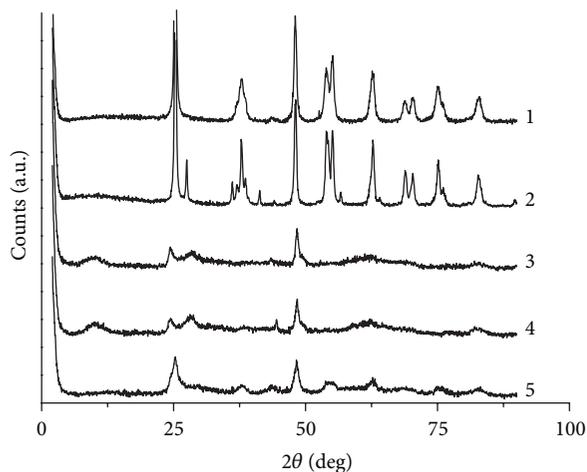


FIGURE 2: XRD of the titanium-containing samples. See Table 1 for the sample code.

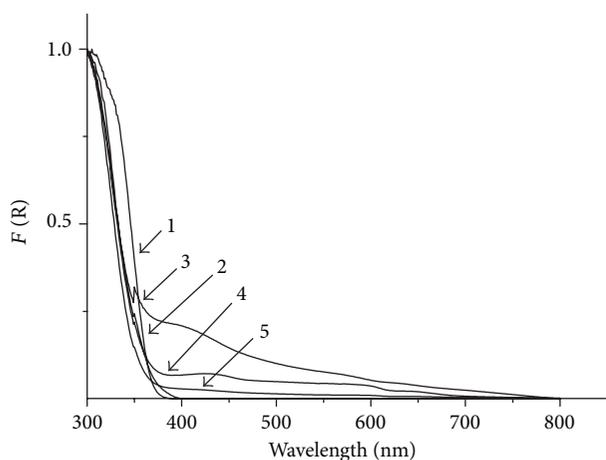
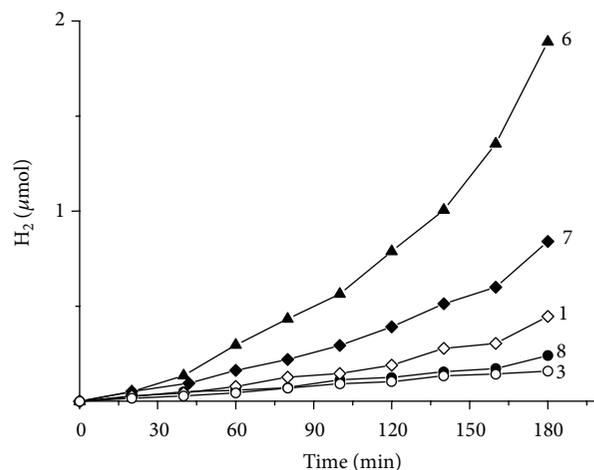


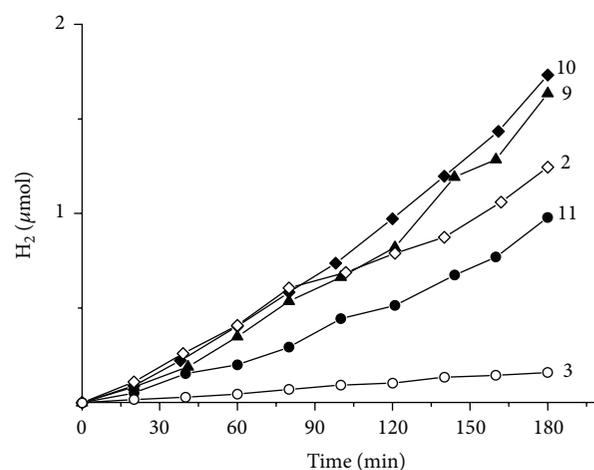
FIGURE 3: Diffuse reflectance UV-Vis absorption spectra (plotted as the Kubelka-Munk function of the remittance (R)) of the set of titanium samples under study. Refer to Table 1 for the sample code.

can exhibit activity for hydrogen generation from water-methanol mixtures with visible light. In the present case, we reasoned that the combination of these titanate nanotubes in a certain percentage with titanium dioxide nanoparticles could lead to an improved photocatalytic system due to the formation of bulk heterojunction, even for different titanium-containing particles.

To test this hypothesis we selected two different commercial titanium dioxide nanoparticles that had been widely used as photocatalysts, for both dye degradation and hydrogen generation, namely, Evonik P25 and Millennium PC500 TiO<sub>2</sub>. To each of these two nanoparticulate titania dioxide samples, increasing proportions of titanate nanotubes from 0 to 100% were added, and the resulting mixtures were evaluated for hydrogen production under ambient conditions using simulated solar light. Figure 4 shows the temporal profiles of hydrogen evolution for some selected mixtures, while Table 1 compiles all the data of hydrogen productivity as a function of the composition of the photocatalyst.



(a)



(b)

FIGURE 4: Photocatalytic hydrogen production from water-methanol (3 : 1) mixtures of selected samples as photocatalysts under simulated sunlight irradiation. Reaction conditions are water-methanol (3 : 1) mixtures 25 mL and catalyst concentration  $1.0 \text{ g} \times \text{L}^{-1}$ . Refer to Table 1 for sample codes and a complete set of hydrogen production values. (a) Samples containing titanate nanotubes and Millennium PC500 TiO<sub>2</sub> particles. (b) Samples containing titanate nanotubes and Evonik P25 TiO<sub>2</sub> particles.

The results indicate that pure Evonik P25 or Millennium PC500 TiO<sub>2</sub> exhibits lower productivity for hydrogen generation than mixtures in which titanate nanotubes are present. The optimal efficiency corresponds to 12% or 6% titanate for Evonik P25 or Millennium TiO<sub>2</sub>, respectively. Interestingly, larger proportion of titanate nanotubes is detrimental for the photocatalytic efficiency.

It should be noted that the results provided in Figure 4 and Table 1 (entries 1–11) correspond to photocatalytic mixture in which platinum or another noble metal was not present. It is well known in the state of the art that the presence of platinum or gold enhances considerably the photocatalytic efficiency of titania by acting as cocatalyst for the evolution of hydrogen gas and by providing the Schottky barrier reducing electron-hole recombination [20, 21]. In

TABLE 1: Code, sample composition, and photocatalytic data of the samples under study.

Sample	Mix composition (wt.%)	H <sub>2</sub> production ( $\mu$ mol) measured at 3 h of solar simulator irradiation
1	100% Millennium PC500 TiO <sub>2</sub>	0.44
2	100% Evonik P25 TiO <sub>2</sub>	1.2
3	100% titanate nanotubes	0.15
4	100% Au NP/titanate nanotubes (0.5 wt.%)	5.10
5	100% Pt NP/titanate nanotubes (0.3 wt.%)	28.8
6	6% of 3 + 94% of 1	1.89
7	12% of 3 + 88% of 1	0.84
8	25% of 3 + 75% of 1	0.24
9	6% of 3 + 94% of 2	1.55
10	12% of 3 + 88% of 2	1.73
11	25% of 3 + 75% of 2	0.97
12	6% of 4 + 94% of 1	6.25
13	12% of 4 + 88% of 1	13.57
14	25% of 4 + 75% of 1	27.92
15	50% of 4 + 50% of 1	29.77
16	6% of 5 + 94% of 1	34.19
17	12% of 5 + 88% of 1	71.87
18	25% of 5 + 75% of 1	137.18
19	50% of 5 + 50% of 1	153.71
20	6% of 5 + 94% of 2	35.46
21	12% of 5 + 88% of 2	74.41
22	25% of 5 + 75% of 2	81.99

view of this, it is also of interest to check whether the synergy that has been observed between titanate nanotubes and titanium dioxide also takes place for samples containing some noble metals as cocatalysts or not. Furthermore, since the amount of noble metals present in the semiconductor should be minimized as much as possible, it is of interest to determine the relative efficiency in terms of the amount of noble metals present in the system.

In order to determine the influence of noble metals on the photocatalytic activity, we prepared titanate nanotubes containing platinum or gold nanoparticles that have been supported by deposition-precipitation method [22, 23] starting from aqueous solution of chloroplatinic or chloroauric acid at pH 10. The platinum or gold content of titanate nanotubes determined by chemical analysis is about 0.3 wt.% and 0.5 wt.%, respectively. These samples containing platinum or gold nanoparticles supported on modified nanotubes were used to prepare mixtures with Evonik P25 and Millennium PC500 titania in proportions ranging from 6 to 100 wt.%. The results of photocatalytic hydrogen generation of these mixtures containing some platinum or gold are also compiled

in Table 1, while Figure 5 shows the temporal evolution of hydrogen under simulated solar light irradiation.

These photocatalytic data of noble metal-containing samples indicate again a synergy due to the combination of the two titanium semiconducting solids. The maximum efficiency with noble metals seems to occur at the highest percentage of platinum containing titanate nanotubes that is observed at 25%, for both Evonik P25 and Millennium PC500 TiO<sub>2</sub>. This optimized efficiency probably reflects that, in addition to the synergy between the two titanium solids, the platinum content is playing an important role as cocatalyst increasing the photocatalytic efficiency. We notice, however, that, even in the case of Millennium PC500 TiO<sub>2</sub>, the platinum content of the optimal photocatalytic mixtures that is present only in the titanate nanotubes is 0.03 wt.% which is significantly low compared to the typical amounts reported for titanium dioxide. For instance, when the photocatalytic efficiency of the titanate nanotubes-titanium dioxide mixtures containing platinum is compared with the best turnover numbers for platinum either deposited on titanate nanotubes or deposited on titanium dioxide, the benefits of the combination of the two different titanium forms can be demonstrated. Thus, the turnover numbers for platinum-Millennium PC500 TiO<sub>2</sub> and platinum-Evonik P25 TiO<sub>2</sub> are 961 and 1892 which are lower than the values of 1831 and 1993 corresponding to platinum for the titanate nanotube-Millennium PC500 nanotubes and platinum for titanate nanotubes-Evonik P25 TiO<sub>2</sub>, respectively.

The synergy between titanate nanotubes and titania nanoparticles can be explained based on related precedents reporting enhanced photocatalytic efficiency of heterojunction of different semiconductors. In agreement with this hypothesis, we propose that light should be preferentially absorbed by titanate nanotubes, since, as shown in Figure 3, this component has absorption beyond 380 nm where anatase does not absorb light. After light absorption in titanate nanotubes, charge separation with the generation of electron and holes would take place. Since the mobility of electron in titania semiconductors is larger than holes, it can be said that conduction band electrons migrate from the site in which they have been generated to the surface of the titanate nanotubes and, then, to the anatase nanoparticle. Interfacial electron migration from the nanotubes to anatase nanoparticles would be the key process enhancing charge separation, minimizing recombination, and extending the lifetime of the charge separated state, as it had been reported for other combinations of semiconductors [24]. This mechanism does not exclude other possibilities taking place independently in each titanium phase but would be unique for the combination of titanate nanotubes with titania nanoparticles, thus resulting in a synergy due to the junction of both phases. Scheme 1 illustrates the mechanistic proposal to rationalize the higher efficiency of the combination of titanate nanotubes with anatase nanoparticles.

#### 4. Conclusions

In the present paper, we provide data showing that the combination of titanate nanotubes, exhibiting an absorption

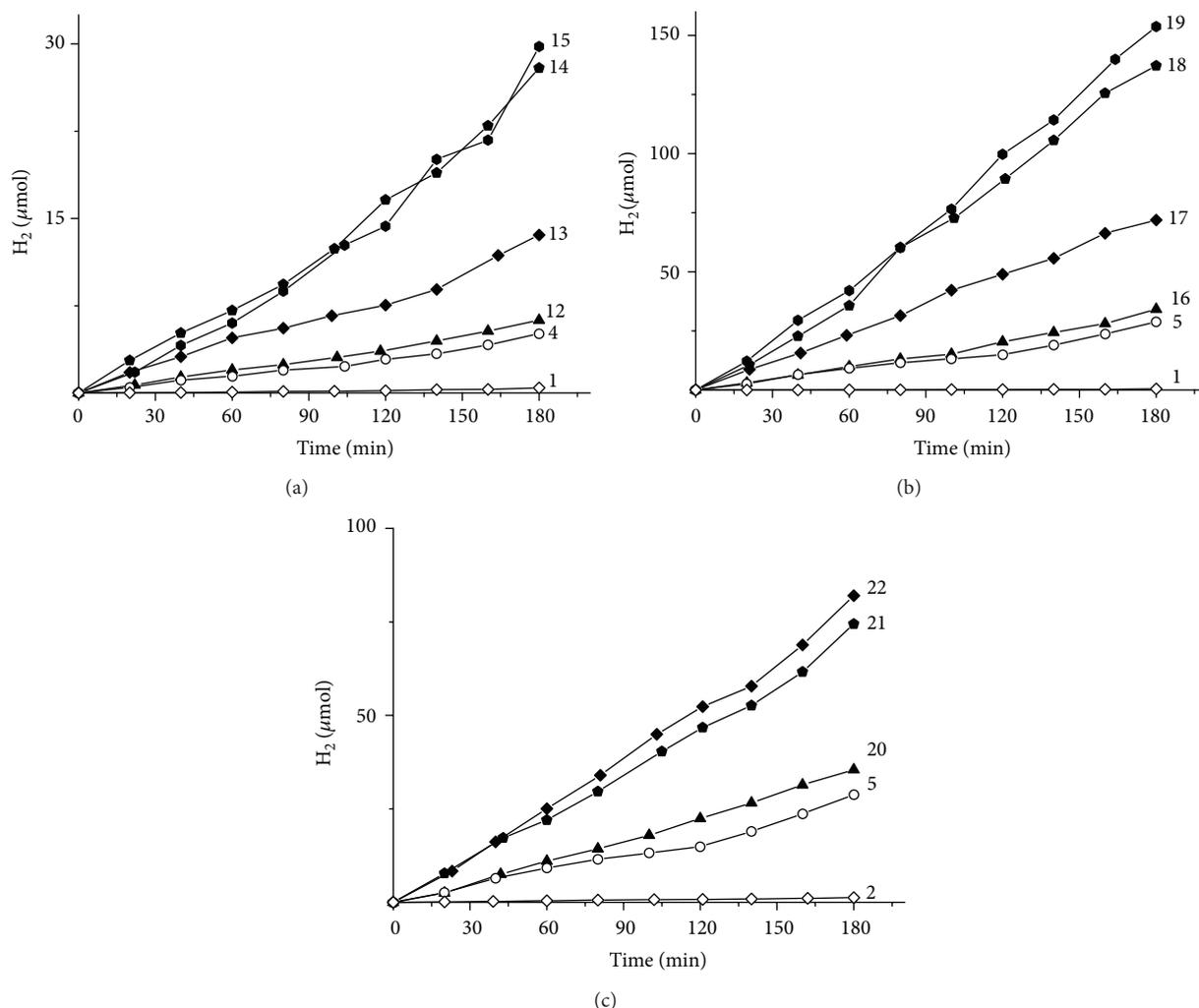
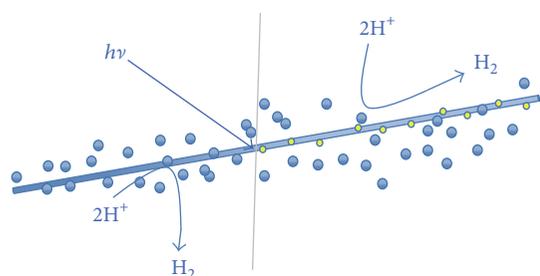


FIGURE 5: Photocatalytic hydrogen production from water-methanol (3:1) mixtures of selected samples as photocatalysts under simulated sunlight irradiation. Reaction conditions are water-methanol (3:1) mixtures 25 mL and catalyst concentration  $1.0 \text{ g} \times \text{L}^{-1}$ . Refer to Table 1 for the sample codes and a complete set of hydrogen production values. (a) Samples containing gold nanoparticles supported on titanate nanotubes and Millennium PC500  $\text{TiO}_2$  particles. (b) Samples containing platinum nanoparticles supported on titanate nanotubes and Millennium PC500  $\text{TiO}_2$  particles. (c) Samples containing platinum nanoparticles supported on titanate nanotubes and Evonik P25  $\text{TiO}_2$  particles.



SCHEME 1: Proposal for the synergy found for the heterojunction of titanate nanotubes (long line) and titania nanoparticles (spheres).

in the visible region, and anatase nanoparticles in the appropriate proportion increases the photocatalytic activity with respect to the activity of the individual components. This

synergetic effect is observed both in the absence and in the presence of noble metals platinum and gold nanoparticles acting as cocatalysts for the hydrogen generation and is proposed to derive from the interfacial electron transfer between the titanate nanotubes and titania nanoparticles; our report complements those that have shown that the morphology of titanium base semiconductors plays a role in the photocatalytic efficiency [25], since, in the present case, we have observed that the combination of two different titanium-based semiconductors with different morphology benefits the photocatalytic activity of the system.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgments

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