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Photocatalytic H₂ Production on Au/TiO₂: Effect of Au Photodeposition on Different TiO₂ Crystalline Phases

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Abstract: In this work, we investigated the role of the crystalline phases of titanium dioxide in the solar photocatalytic H₂ production by the reforming of glycerol, focusing the attention on the influence of photodeposited gold, as a metal co-catalyst, on TiO₂ surface. We correlated the photocatalytic activity of 1 wt% Au/TiO₂ in anatase, rutile, and brookite phases with the structural and optical properties determined by Raman spectroscopy, N₂ adsorption–desorption measurements, UV–vis Diffuse Reflectance Spectroscopy (UV–vis DRS), X-ray photoelectron spectroscopy (XPS), Photoluminescence spectroscopy (PL), and Dynamic Light scattering (DLS). The best results (2.55 mmol H₂ g_{cat}^{−1} h^{−1}) were obtained with anatase and gold photodeposited after 30 min of solar irradiation. The good performance of Au/TiO₂ in anatase form and the key importance of the strong interaction between gold and the peculiar crystalline phase of TiO₂ can be a starting point to efficiently improve photocatalysts design and experimental conditions, in order to favor a green hydrogen production through solar photocatalysis.

Keywords: hydrogen; photoreforming; titanium dioxide; glycerol; photocatalysis; gold



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1. Introduction

Nowadays, the transition towards a more carbon-free society is a key point of technological and socio-economic progress. The environmental concerns related to the depletion of natural resources and atmospheric pollution require sustainable and green solutions. The development of new technologies based on renewables is the main road to drive the environmental transition. In this context, hydrogen is a promising energy carrier and can be the leading actor of the green innovation [1]. Unfortunately, until now, hydrogen has been mostly produced in a not sustainable way, namely, through the steam reforming of hydrocarbons, which requires fossil fuels and causes relevant CO₂ emissions [2].

In the last years, photocatalytic hydrogen production has received increasing attention due to its green potentiality. Since the pioneering work of Fujishima and Honda in the 1972 [3], scientific research has focused its attention on photocatalytic hydrogen production by water splitting or photoreforming of organic substrates [4,5]. This latter process is promising for a carbon-neutral vision, because the obtained CO₂ can be easily reconverted, even through the solar photocatalytic process, in bio-substrates [6]. Therefore, the sustainability of the process strongly depends on the choice of the organic substrates [7]. Many works reported the use of alcohols such methanol or ethanol or acids such as lactic or acetic acid, or also carbohydrates such as glucose as substrates [8–11].

Recently, the valorization of glycerol has attracted a growing interest, due to its large production as a by-product of biodiesel [12]. Furthermore, the photoreforming of glycerol (Reaction (1)) allows obtaining a high amount of hydrogen for each glycerol molecule [13,14].



The most used semiconductor material in photocatalysis is certainly titanium dioxide (TiO_2 , titania). It has been largely investigated since the 1970s and is used in many applications [15–19]. It exists in three principal crystalline phases: anatase, rutile, and brookite. The first one is the most used in photocatalysis thanks to its chemico-physical properties [20]. Anatase has a tetragonal arrangement, is stable at room temperature, and is also the least dense among the three phases; this favors the mobility of charge carriers (photoelectrons and photoholes), which is an important parameter that explains its large use in photocatalysis [20]. Similar to the anatase, also the rutile phase has a tetragonal arrangement; however, it is more packed compared to anatase and thus generates a greater thermodynamic stability but also a greater density [21]. Finally, brookite is the least investigated crystalline form of TiO_2 due to its low stability and the difficulty to obtain it as a pure phase. Brookite possesses an orthorhombic arrangement and an intermediate density amongst those of the three TiO_2 crystalline forms (3.7 g/cm^3 for anatase, 4.23 g/cm^3 for rutile, and 4.12 g/cm^3 for brookite) [22].

The photocatalytic activity of TiO_2 is strongly affected by two important issues: poor visible light absorption and high charge carrier recombination rate [23]. For these reasons, the presence of a co-catalyst, generally a noble metal, is usually required for photocatalytic hydrogen production. Many works reported that the presence of these metals on the surface of semiconductors promotes hydrogen evolution because they play the role of charges “accumulators”, being centers of electrons release necessary for proton reduction [24]. This leads to an improved charge carrier separation and to a higher photocatalytic activity.

Among the noble metals, gold also allows exploiting its surface plasmon resonance (SPR) effect that enhances visible light absorption and charges generation around the TiO_2 surface [25–30]. Furthermore, as reported [31–33], the combination of a good interaction between gold and TiO_2 and the Au SPR effect allowed obtaining a high photocatalytic H_2 production under solar/visible irradiation, sometimes higher than that obtained with the other noble metal co-catalysts used for this reaction, such as Pt, Pd, or Ag. Finally, the chemico-physical properties of gold can be more easily tuned compared to those of the other noble metals, depending on the particular preparation method employed for gold deposition, i.e., deposition–precipitation, sol–gel, laser ablation, colloidal impregnation, etc. [31]. All these features make gold an ideal co-catalyst for TiO_2 for the photoreforming and water splitting reactions.

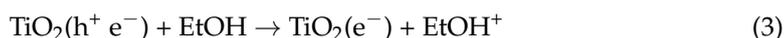
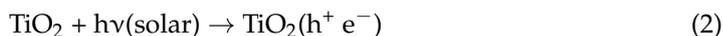
On the basis of the above considerations, in our work, we investigated hydrogen evolution through the photoreforming of glycerol using Au/ TiO_2 photocatalysts prepared by photodeposition of gold on the three crystalline phases of TiO_2 . We explored in detail the modifications of the structural and optical properties due to gold photodeposition on the TiO_2 phases and how these modifications affected the photocatalytic H_2 evolution. The main novelty of the present work is the focus on the parameters that influence gold photodeposition on the different TiO_2 polymorphs and their correlation with the photocatalytic activity in the photoreforming reaction. The solar photodeposition here proposed, can be considered an easy and sustainable route to prepare gold-based photocatalysts; it does not require peculiar thermal treatments or the use of expensive or toxic chemicals. Furthermore, it is also characterized by a high versatility: indeed, the same photoreactor can be used for both the materials’ synthesis and the photocatalytic tests.

2. Materials and Methods

2.1. Samples Preparation

Anatase, rutile, and brookite, titania were used as purchased (Sigma-Aldrich, Buchs, Switzerland). Tetrachloroauric acid (HAuCl_4 , Merck KGAA, Darmstadt, Germany) was solubilized in water, and a 5 g/L solution was used as a precursor of gold co-catalysts. For gold deposition, the method described by Williams G., Seger B., and Kama P. [34] was slightly modified. In a typical procedure, 0.2 g of TiO_2 powder was suspended in 35 mL of ethanol and put in a home-made jacketed batch Pyrex reactor, keeping the stirring at 800 rpm and the temperature at $25 \text{ }^\circ\text{C}$. Then, a stoichiometric amount of HAuCl_4 (to obtain

a final Au content of 1 wt%) was added, and the suspension was purged with argon for 1 h in order to remove the oxygen inside the reactor. Then, a solar lamp (OSRAM Vitalux, OSRAM Opto Semiconductors GmbH, Leibniz, Regensburg Germany, 300 W, irradiance of 10.7 mW/cm²) was turned on for 30 min. This irradiation process generated the charge carriers (photoelectrons and holes) on TiO₂. The holes were scavenged by ethanol, whereas the photoelectrons were able to reduce the Au³⁺ ions. This process can be summarized with the following reactions:



Finally, the obtained powders were centrifuged and dried in an oven at 70 °C for 12 h. For comparison, bare titanium dioxide samples were used as purchased. Furthermore, for the most performing phase, the Au content and the time of irradiation in the photoreduction process were modified in order to find the best experimental conditions that promoted the final photocatalytic activity.

2.2. Samples Characterizations

The textural properties of the samples were analyzed by N₂ adsorption–desorption isotherms, carried out with a Micromeritics Tristar II Plus 3020 (Micromeritics Instrument Corp., Norcross, GA, USA) after an outgassing at 60 °C overnight. The Braunauer–Emmet–Teller (BET) theory, for the determination of the surface area, and the Barret–Joyner–Halenda (BJH) theory, for the determination of pore size distribution, were applied. The optical properties of the samples were investigated by UV–vis DRS (Diffuse Reflectance Spectroscopy), carried out with a JASCO V-670 (Jasco Europe S.R.L., Cremella, Italy) equipped with an integration sphere and using barium sulphate as a reflectance standard. The optical band gaps were estimated with the TAUC plot according with the Kubelka–Munk theory [35]. Dynamic Light Scattering (DLS) measures were carried out with a HORIBA (Horiba UK Limited, Kyoto Close, Moulton Park, Northampton, UK) Scientific nano particle analyzer SZ-100 in disposable PMMA cuvettes. Raman spectra were acquired by a WITec alpha 300 confocal Raman system (WITec Wissenschaftliche Instrument und Technologie GmbH, Ulm, Germany) with the experimental conditions described in the ref. [11]. X-ray photoelectron spectroscopy (XPS) was carried out with a K-Alpha X-ray photoelectron instrument (Thermo Fisher Scientific, Waltham, MA, USA), using the carbon 1s band at 284.9 eV (due to adventitious carbon) as a reference. Photoluminescence spectroscopy (PL) was performed with a Perkin Elmer LS45 luminescence Spectrometer (Perkin Elmer, Inc., Waltham, MA, USA).

2.3. Photocatalytic Experiments

The photocatalytic tests were performed using the same Pyrex jacketed batch reactor and solar lamp employed for sample preparation. In these experiments, 50 mg of powder was suspended in 50 mL of a water–glycerol solution (45 mL and 5 mL respectively) under constant stirring at 800 rpm, and the temperature was kept at 35 °C. The suspension was purged 1 h with argon, and then the solar lamp was turned on for 4 h. The amount of hydrogen produced was evaluated with a gas chromatograph (Agilent 6890, Agilent Technologies, Santa Clara, CA, USA) equipped with a packed column (Carboxen 1000) and a TCD detector. Argon was used as the gas carrier. For H₂ quantification, a 0.5 mL aliquot of reaction gases was withdrawn using a syringe (Hamilton Gastight 1001, Hamilton, Bonaduz AG, Switzerland) and injected in the GC. For the reusability tests, after each run, the photocatalyst was centrifuged, washed with water, dried at room temperature, and then re-used.

3. Results and Discussion

3.1. Photocatalytic Activity

Figure 1 reports the photocatalytic activity data related to hydrogen evolution over the investigated TiO₂ and Au/TiO₂ samples. The best result was obtained with the Anatase–Au sample, which produced 2.55 mmol g_{cat}^{−1} h^{−1} of hydrogen after 4 h of solar light, followed by the Brookite–Au and Rutile–Au samples (2.01 and 0.38 mmol g_{cat}^{−1} h^{−1}, respectively). As expected, the bare oxides (anatase, brookite, and rutile) were almost inactive in the solar photoreforming reaction. Interestingly, for all the three TiO₂ phases, the addition of gold resulted in a significant increase of H₂ evolution (more than 60 times) compared to that achieved with the unmodified oxides. The interaction between gold and TiO₂ was better exploited when TiO₂ was in anatase form, whereas rutile TiO₂ gave the lowest photoactivity. This was in accordance with previous literature reports, pointing to the anatase form as the best supported phase for gold [36,37].

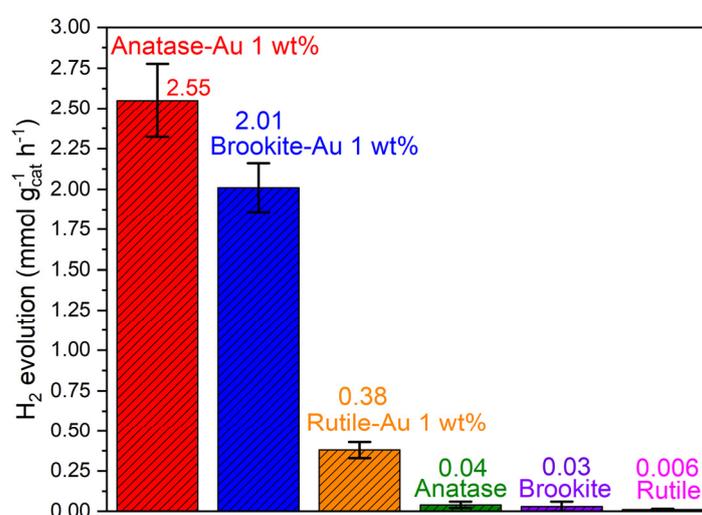


Figure 1. Hydrogen evolution on the investigated samples after 4 h of solar irradiation.

Figure 2 reports the trend of the photocatalytic activity as a function of the gold content on anatase. In this case, it is clear how, in our experimental conditions, the optimal amount of gold was 1 wt%.

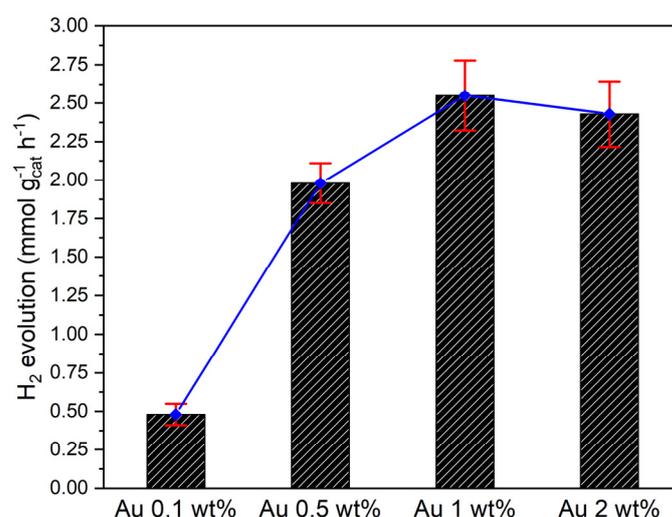


Figure 2. Influence of the amount of gold deposited on anatase TiO₂ versus H₂ production.

This behavior can be rationalized considering that with photodeposition here used to prepare the Au/TiO₂ samples, an amount of gold higher than 1% can be detrimental, leading to an agglomeration of gold particles [38]. Moreover, a higher concentration of gold precursor resulted in a lower Au reduction efficiency in the photodeposition process [38]. However, considering the high cost of gold, the use of a relative low Au amount (0.5 or 1 wt%) can be highly positive in terms of the overall process sustainability.

Another key parameter of the photodeposition technique is the time of irradiation/deposition employed in the preparation of the supported Au photocatalysts. Table 1 summarizes the evolution of H₂ amounts on 1 wt% Au/TiO₂ anatase samples varying the solar irradiation times.

Table 1. Different irradiation–deposition times during the preparation of 1 wt% Au/TiO₂ anatase and their effect on the photocatalytic activity.

Irradiation Time [min]	H ₂ Amount [mmol g _{cat} ⁻¹ h ⁻¹]
15	2.24 ± 0.21
30	2.55 ± 0.24
45	2.14 ± 0.19
60	1.83 ± 0.16

It is possible to note that the best photocatalyst was obtained with an irradiation time of 30 min. Reasonably, lower times were not sufficient to reduce all the gold precursor, whereas higher times favored the agglomeration of gold particles.

Reusability tests were carried out to check the stability of the Anatase–Au 1 wt% sample, and the results are shown in Figure 3a,b. At the end of each run, the sample was centrifuged, dried at room temperature, and re-used without thermal treatments.

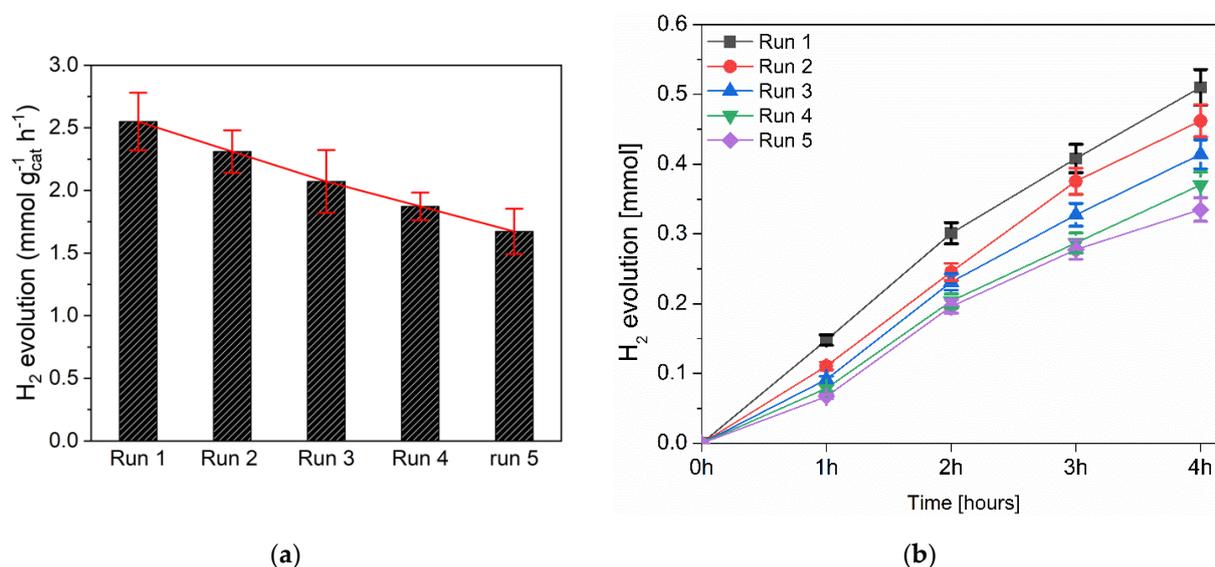


Figure 3. (a) Photocatalytic activity of Anatase–Au 1 wt% on five subsequent runs, (b) H₂ evolution in each hour of the stability tests.

The catalytic stability of Au/TiO₂ anatase was good until the third run; afterwards, there was a more substantial decrease of H₂ production, and in the fifth run, the photoactivity decreased by about 30% compared to the first run. The activity loss can be reasonably ascribed to the difficulty to recover all the powders after each consecutive test. However, a loss of efficiency due to the progressive aggregation of the gold particles on the surface of TiO₂ as a consequence of protracted solar irradiation cannot be excluded [39].

3.2. Samples Characterization

Figure 4 shows the UV–vis DRS spectra of the investigated samples (a) and the corresponding TAUC plots determined with the Kubelka–Munk function (b) to estimate the optical band gap of the samples.

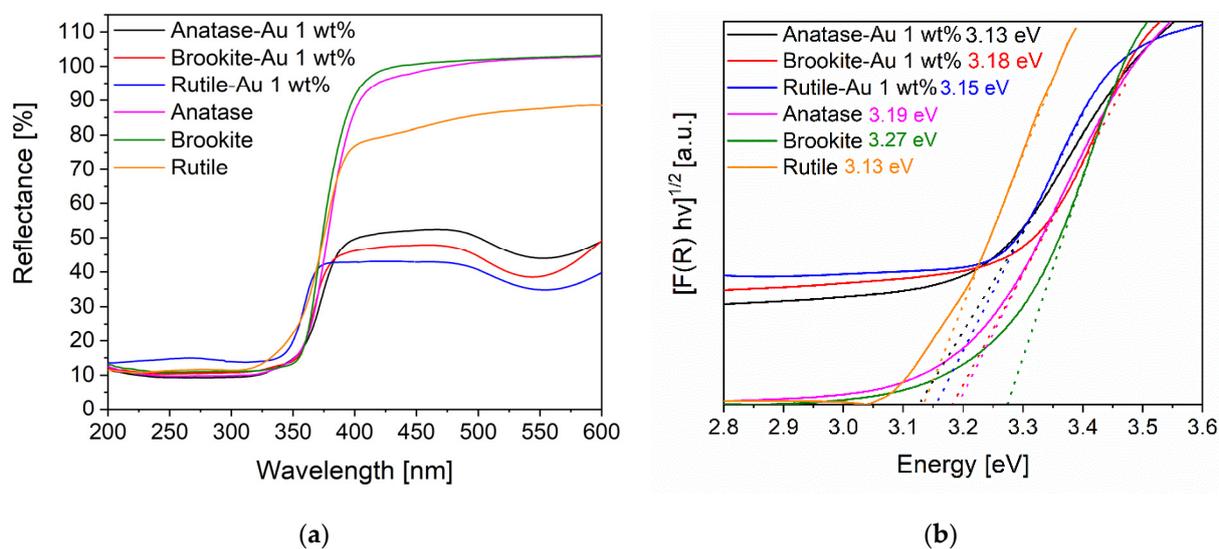


Figure 4. (a) UV–vis DRS measurements in R%, (b) Kubelka–Munk functions for the estimation of the optical band gap of the investigated samples.

No significant differences in the UV–vis DRS spectra were detected among the three TiO₂ phases, whereas for all the gold-based samples, the presence of the surface plasmonic resonance (SPR) band of gold was evident at around 550 nm. This additional light absorption in the visible portion can be one of the crucial features that explain the significant enhancement of the photocatalytic activity due to the addition of gold on TiO₂. Furthermore, on anatase and brookite samples, the presence of gold determined a slight decrease of the band gap values (Figure 4b) compared to those of the corresponding unmodified oxides. On the contrary, the rutile-based Au sample showed similar values as bare rutile, indicating the smallest interaction between gold and TiO₂ in the rutile phase, as also confirmed by the photocatalytic data. The SPR band was at 552 nm for the Au/TiO₂ anatase, at 554 nm for the Au/TiO₂ rutile, and at 542 nm for the Au/TiO₂ brookite. This indicated that Au particle size was in the range 5–10 nm [37,40]. The correlation between the SPR band and gold size is influenced by the dielectric constant of the surrounding medium [37,40]; therefore, when gold is deposited on an oxide (such as TiO₂), the wavelength of SPR is almost independent of Au particle size, contrary to what observed for unsupported gold (e.g., present as a colloidal solution). For the Au/TiO₂ samples, the optical features of gold as well as the final photocatalytic H₂ production were mainly related to the strength of the metal–support interaction.

The Raman spectra of the Au/TiO₂ samples are reported in Figure 5. Gold deposition on titania surface did not change the crystalline structures of the bare oxides, being the spectra similar to those of pure anatase, rutile, and brookite, respectively (Figure S1).

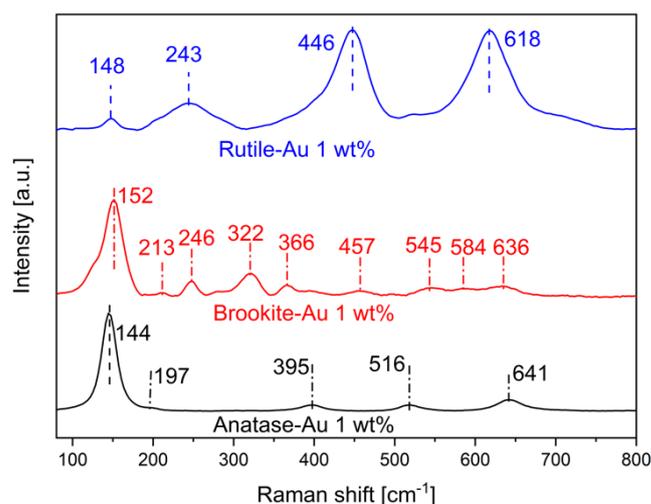


Figure 5. Raman spectra of the samples containing the gold particles.

In particular, for the anatase phase, we observed signals at 144 cm^{-1} , 197 cm^{-1} , 395 cm^{-1} , 516 cm^{-1} , and 641 cm^{-1} , related to E_g , E_g , B_{1g} , $A_{1g} + B_{1g}$, and E_g , vibrational modes, respectively [41]. Regarding the rutile form, four different signals were detected at 148 cm^{-1} , 446 cm^{-1} , 618 cm^{-1} , and 243 cm^{-1} , assigned to the B_{1g} , E_g , A_{1g} modes and to a multi-phononic process, respectively [42]. Finally, a multitude of modes were detected in the brookite phase, assigned to A_{1g} (152 cm^{-1} , 246 cm^{-1} , 636 cm^{-1}), B_{1g} (213 cm^{-1} , 322 cm^{-1}), B_{2g} (366 cm^{-1} , 457 cm^{-1} , 584 cm^{-1}), and B_{3g} (545 cm^{-1}) [43]. The pure brookite phase was verified by the presence of the typical band at 152 cm^{-1} and the absence of the vibrational mode at 516 and 446 cm^{-1} of anatase and rutile, respectively.

The DLS (Dynamic Light Scattering) and N_2 adsorption–desorption results for the investigated samples are reported in Table 2. Interestingly, a correlation existed between these features and the photocatalytic activity. In fact, the anatase phase showed the highest value of BET surface area ($53\text{ m}^2/\text{g}$), followed by the brookite ($46\text{ m}^2/\text{g}$) and finally by the rutile ($38\text{ m}^2/\text{g}$) phases. In accordance, the DLS values ascribed to the hydrodynamic radius of the Au/TiO₂ samples followed a reverse trend compared to the surface area, being 184 nm , 200 nm , and 840 nm , for anatase, brookite, and rutile, respectively, similar to those of the bare oxides. As largely reported in the literature [44,45], a high surface area, in this case also favored by a small hydrodynamic radius, favors photocatalytic H₂ production, being this a surface reaction. This is another important feature that allowed obtaining the highest H₂ evolution on the Au/TiO₂ anatase sample. This sample, in fact, showed the highest surface area and the lowest hydrodynamic radius.

Table 2. Hydrodynamic radii, surface areas, and mean pore diameters of the investigated samples.

Samples	DLS ¹ (nm)	S _{BET} (m ² /g)	d _p ² (nm)
Anatase	186	53;	20
Rutile	820	38	24
Brookite	210	46	24
Anatase–Au 1 wt%	184	55;	20
Rutile–Au 1 wt%	840	40;	25
Brookite–Au 1 wt%	200	49	24

¹ Hydrodynamic radius measured by Dynamic Light Scattering. ² Average pore diameters determined with the Barret–Joyner–Halenda (BJH) method.

An interesting aspect is related to the BET surface area values after gold photodeposition, which slightly increased, probably thanks to the partial surface reduction of titania, as also observed previously, adopting the same photoreduction synthesis [46]. Finally, no par-

ticular variations were detected in the samples regarding the pore size. All photocatalysts were mesoporous, with pores in the range of 20–25 nm.

The surface properties of the Au/TiO₂ samples determined by x-ray photoelectron spectroscopy (XPS) are reported in Table 3 and Figure S2. For all samples, the Au 4f_{7/2} and the Au 4f_{5/2} spin-orbit components located at about 83.6 eV and 87.3 eV, respectively, were the typical signals of the Au⁰ state [47], pointing to a complete photoreduction of the gold salt precursor on the surface of TiO₂ (see page 3, Reactions (2)–(4)). The measured surface content of gold was similar (0.84–0.86 wt%) to the nominal one (1 wt%), highlighting that all the deposited gold was on the surface of TiO₂. The Ti 2p bands located at 458.8 eV and 464.8 eV for the anatase–Au sample were ascribed to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, and are the fingerprints of Ti⁴⁺ in a tetragonal structure [48]. Consequently, the rutile–Au sample showed similar bands, whereas for the brookite–Au catalyst, these bands were slightly shifted (459.1 eV and 465.1 eV, respectively) due to the orthorhombic arrangement of brookite [49]. Finally, in the O 1s region, the band at about 530 eV and the component at about 532 eV were assigned to lattice oxygen in TiO₂ and to surface oxygen of hydroxyl species [50]. No significant differences were detected in the Ti and O regions considering the bare TiO₂ supports.

Table 3. XPS analysis of the Au-based samples.

Sample	Au 4f BE	Au Content (wt%)	Ti 2p BE	O 1s BE
Anatase–Au	83.6;87.3	0.86	458.8;464.8	529.9;531.6
Rutile–Au	83.6;87.3	0.84	458.9;464.9	530.3;532.6
Brookite–Au	83.6;87.3	0.84	459.1;460.0	530.8;531.9

3.3. Strong Metal Support Interaction (SMSI) between Gold and TiO₂

The photodeposition of gold on TiO₂ gave the best results with the anatase phase, a gold content of 1 wt%, and a time of irradiation/deposition of 30 min. Under these experimental parameters, a satisfactory H₂ production was obtained, which was higher or comparable to those of the other Au/TiO₂-based samples reported in the literature for the solar/visible photoreforming reaction (Table 4), although an accurate comparison is very difficult due to the various experimental conditions adopted by different research groups.

On the basis of the results of this work and of those reported in the literature [51–56], it is clear that the good interaction between gold and anatase favored H₂ evolution, and this is the most important feature that directly affects H₂ production, whereas the gold particle size played a minor role. This differentiates the catalytic behavior of gold-based samples in photocatalysis. Conversely, indeed, in thermocatalytic applications, the gold dimensions are crucial in order to have a good activity [57,58]. Moreover, the use of TiO₂ with a mixed phase (TiO₂ P25 is the most used “standard” sample, where however the anatase (80%) is preponderant with respect to the rutile (20%) phase) did not substantially improve H₂ evolution, being the values reported in the literature (Table 4) similar to or lower than those of the Au/TiO₂ anatase samples, as confirmed also in our experimental conditions, where the Au/TiO₂ P25 photocatalyst, prepared with the same experimental procedures reported in the Section 2.1 gave an H₂ production of 2.49 mmol g^{−1} h^{−1}, slightly lower than that of Au/TiO₂ anatase (2.55 mmol g^{−1} h^{−1}).

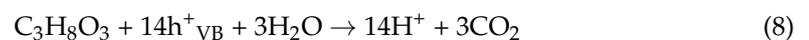
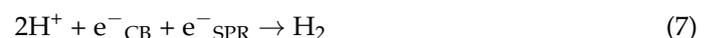
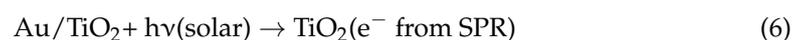
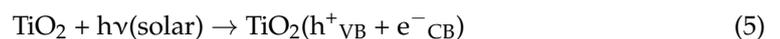
Table 4. Comparison of the solar/visible hydrogen evolution data from photoreforming on various Au/TiO₂-based samples.

Sample	Gold Deposition Method and Au Size	H ₂ Evolved ¹	Photocatalytic Conditions ²	Ref.
1 wt% Au/TiO ₂ anatase	Photodeposition, 5–10 nm	2.5	300 W solar lamp; 5 mL glycerol	this work
2 wt% Au/TiO ₂ anatase	Deposition–precipitation, 6 nm	0.4	Natural sunlight; 5 mL ethanol	[52]
1 wt% Au/TiO ₂ anatase	Sol-gel, 70 nm	2.0	500 W tungsten halogen lamp with a cut-off filter ($\lambda > 400$ nm), 10 mL isopropanol	[53]
2 wt% Au/TiO ₂ P25	Wet impregnation, 10 nm	2.7	300 W solar lamp; 10 mL methanol	[54]
0.94 wt% Au/TiO ₂ P25	Sol immobilization, 9 nm	1.2	Vis. Light filtered 400–700 nm; 5 mL methanol	[55]
0.5 wt% Au/TiO ₂ P25	Solid grinding, 23 nm	0.5	150 W Ceramic-Metal-Halide Lamp (solar light simulation), methanol 1% vol.	[56]

¹ Amount in mmol g_{cat}⁻¹ h⁻¹; ² irradiation source and sacrificial agent used in the photocatalytic experiments.

The here investigated photodeposition method led to a strong metal–support interaction (SMSI) with the anatase phase, with respect to the brookite and rutile phase. The higher hydrodynamic radius and the lower surface area of these latter crystalline phases compared to those of anatase did not favor an efficient gold deposition, thus explaining the lower activity. On the contrary, with the anatase, the combination of a high SMSI and an increased solar photoactivity, caused by the surface plasmon resonance effect of gold, resulted in a good H₂ production. Furthermore, as confirmed by the literature data (Table 4), the photocatalytic activity did not seem to be correlated with gold dimensions but appeared to be driven by the interaction between the gold co-catalyst and the TiO₂ crystalline phase.

Figure 6 shows the proposed reaction mechanism considering the obtained data. In particular, the UVA portion (in accordance with the obtained optical bandgap values) of solar irradiation led to the formation of holes (h⁺) and photoelectrons in the valence (VB) and in the conduction (CB) bands of TiO₂, respectively, (Reaction (5)). The visible light portion of solar irradiation activated the surface plasmon resonance effect of gold deposited on the surface of TiO₂, and allowed the injection of further electrons in the conduction band of TiO₂ (Reaction (6)). In this way, the photoelectrons and the electron coming from the Au SPR were able to efficiently reduce the proton from water (Reaction (7)), whereas the holes oxidized glycerol (hole scavengers), promoting the photoreforming (Reaction (8)) as well as the oxidation of water (Reaction (9)) [26,59]. In this way, charge carrier recombination (a common reason of photocatalysts deactivation) was strongly reduced, improving H₂ evolution.



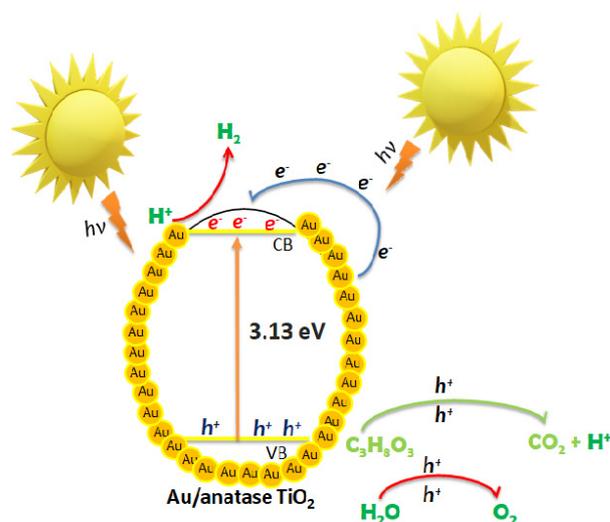


Figure 6. Proposed reaction mechanism.

The charge carrier separation was also improved by the presence of gold on TiO_2 . This was verified by photoluminescence (PL) characterization, whose results are illustrated in the Figure 7. All samples showed four bands related to the band-to-band emission of TiO_2 (388 nm), the self-trapped excitons localized on the surface of titania (420 nm), and the presence of oxygen vacancies and defects in TiO_2 (485 and 525 nm) [60,61]. It is possible to note that the presence of gold led to a decrease of the intensity of these bands and that the Au/anatase TiO_2 sample showed the lowest PL bands intensity. A lower PL intensity is generally related to a lower recombination rate of light-generated charge carriers [61], confirming that with the anatase form, the strong interaction with gold allowed a better improvement of charge carrier separation compared to Au/brookite TiO_2 and Au/rutile photocatalysts. This is another key feature that clarifies the higher H_2 production obtained with the gold/anatase sample with respect to the other investigated powders.

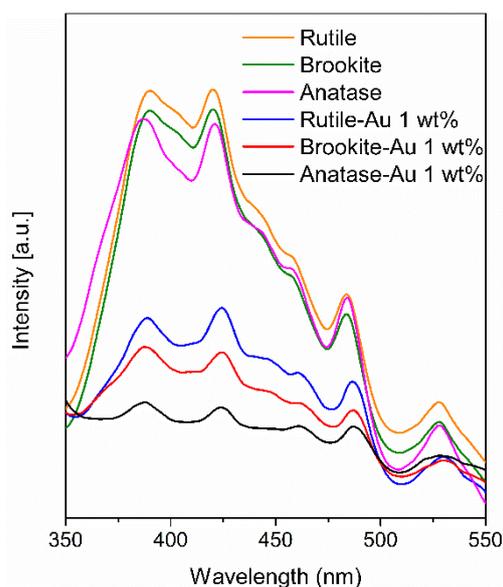


Figure 7. Photoluminescence spectra of the analyzed samples (excitation wavelength of 320 nm).

Finally, compared to the other preparation methods used for the preparation of gold/titania photocatalysts, such as deposition-precipitation, laser ablation, sol-gel, etc. [51,62], photodeposition certainly is an easy one-step preparation technique that avoids the addition of other chemicals and thermal treatments and that owns a promising versatility for possible

scale-up applications. In fact, the photoreactor can be used for both materials synthesis and photocatalytic tests. Furthermore, the use of glycerol as a sustainable organic substrate of photoreforming and the exploitation of solar light are promising aspects that will provide a high sustainability of the overall process for green hydrogen production.

4. Conclusions

In this work, we investigated the performance in hydrogen evolution from solar photoreforming of glycerol of Au/TiO₂ samples prepared through the photodeposition of gold on different titanium dioxide phases. Very promising results were obtained using the anatase phase, with 2.55 mmol g_{cat}⁻¹ h⁻¹ of evolved hydrogen. The rutile phase showed the lowest photocatalytic activity due to its biggest hydrodynamic radius and lowest surface area compared to the anatase and brookite phases, which inhibited the interaction with gold. The best amount of gold was 1 wt% on TiO₂ anatase. The solar photodeposition method is promising for gold deposition on a semiconductor surface avoiding expensive procedures and thermal treatments. Finally, the use of solar light efficiently activated the gold surface plasmon resonance effect, with the double positive effect of favoring the interaction with anatase and the absorption of solar light, boosting up H₂ production.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/j5010006/s1>, Figure S1: Raman spectra of bare anatase, rutile, and brookite TiO₂; Figure S2: XPS spectra of the analyzed samples.

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