A Cocatalytic Electron Transfer Cascade Site-Selectively Placed on TiO₂ Nanotubes Yields Enhanced Photocatalytic H₂ Evolution

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Separation and transfer of photo-generated charge carriers are key elements in designing photocatalysts. TiO_2 in numerous geometries has been for many years the most studied photocatalyst. To overcome kinetic limitations and achieve swift charge transfer, TiO_2 has been widely investigated with cocatalysts that are commonly randomly placed nanoparticles on a TiO_2 surface. The poor control over cocatalyst placement in powder technology approaches can drastically hamper the photocatalytic efficiencies. Here in contrast we show that the site-selective placement of suitable charge-separation and charge-transfer cocatalysts on a defined TiO_2 nanotube morphology can provide an enhancement of the photocatalytic reactivity. We design with nanoscale precision a TiO_2 - WO_3 -Au electron transfer cascade photocatalyst for H_2 production on TiO_2 nanotube arrays. Key aspects in the construction are the placement of the WO_3 /Au element at the nanotube top by site-selective deposition and self-ordered thermal dewetting of Au. In the ideal configuration, WO_3 acts as buffer layer for TiO_2 conduction band electrons, allowing for their efficient transfer to the Au nanoparticles and then to a suitable environment for H_2 generation, while TiO_2 holes due to intrinsic upward band bending in the nanotube walls and short diffusion length undergo a facilitated transfer to the electrolyte where oxidation of hole-scavenger molecules takes place. These photocatalytic structures can achieve H_2 generation rates significantly higher than any individual cocatalyst- TiO_2 combination, including a classic noble metal- TiO_2 configuration.

1. Introduction

In 1972 Fujishima and Honda demonstrated the feasibility of water splitting at the surface of an illuminated rutile TiO_2 single crystal photo-anode.^[1] Since then TiO_2 became the most investigated photocatalyst, and was demonstrated to be able to split H_2O into H_2 and O_2 also under “open circuit conditions”.^[2] H_2 evolution is enabled owing to TiO_2 semiconductive behavior ($E_{g \text{ TiO}_2} \sim 3.0\text{-}3.2 \text{ eV}$) and to its favorable band edge positions. The TiO_2 conduction band (CB) minimum lies above the $\text{H}_2\text{O}/\text{H}_2$ redox potential (-0.45 and 0 V vs. NHE ,

respectively, at pH 0^[3]) and thus under UV light irradiation, photopromoted electrons in TiO₂ CB can reduce H₂O to H₂.

In spite of the favorable thermodynamic situation, pristine TiO₂ typically shows low efficiencies for H₂ generation. The reason is not only that photo-generated charge carriers are subject to trapping and recombination in the semiconductor, but also that the electron transfer to the reactants is slow (i.e. shows a sluggish kinetics) – this in any aqueous media with or without sacrificial agent.^[4,5]

Significantly higher photocatalytic performances can be attained by (i) the use of nanostructured TiO₂ (providing short diffusion length for charge carriers, intrinsically favorable charge separation pathways, high surface area) and (ii) the modification of the photocatalyst with a suitable cocatalyst.

Cocatalysts are mainly based on two principles: TiO₂ can be combined with a second semiconductor (junction-type) having suitable band edge positions (the hetero-junction aids separating carriers before they recombine) or with a charge-transfer cocatalyst such as noble metal nanoparticles (Au, Pt, Pd) that trap TiO₂ CB electrons and mediate their transfer to reactants.

Countless examples for TiO₂ nanostructures combined to a suitable cocatalyst exist. A particularly interesting case is WO₃, which is an n-type semiconductor with a band gap E_g WO₃ ~ 2.6-2.8 eV.^[6-8] Particularly in photocatalytic oxidation reactions, combined Ti-W oxides can under optimized conditions outperform the individual oxides.^[9-12] The reason is the favorable conduction band alignment at the TiO₂-WO₃ interface that leads to more efficient charge separation since TiO₂ CB electrons diffuse into the WO₃ CB. Holes in TiO₂ thus have a longer lifetime and become more readily available for a reaction.

For classic charge transfer cocatalysts, TiO₂ nanostructures are typically modified with noble metal nanoparticles such as Au or Pt.^[4,5,13]

Nevertheless, only comparably few works show the combination of the two principles, e.g. a TiO_2 - WO_3 -noble metal combination, in spite of the potential beneficial effect.

For example, Pap *et al.* synthesized TiO_2 - WO_3 -noble metal (Au or Pt) powders by noble metal photo-deposition on either TiO_2 or WO_3 .^[14] Then, the other (pristine) oxide was added to the noble metal-modified one. Their work shed light on the potential of a combined effect of two cocatalysts but the chosen photocatalyst preparation led only to poor control over morphology and stacking of the cocatalysts and probably also to a loose and undefined contact (junction) between the two oxides – this is due to the use of a powder technology approach. Such a poor morphological control was shown to strongly limit the photocatalytic performance: any noble metal- WO_3 - TiO_2 combination was found significantly less active for H_2 evolution than the classic and well-established noble metal- TiO_2 configuration.

In the present work we in contrast design a synergistic photocatalytic platform by constructing a geometrically well-defined electron transfer cascade from TiO_2 nanotubes arrays. These TiO_2 nanotube (NT) arrays have attracted wide attention in the last decades^[15,16] as they can be fabricated by simple anodization of Ti metal in a suitable electrolyte under self-organizing electrochemical conditions. The use of vertically aligned tubes allows to construct a highly-defined WO_3 junction as well as the placement of a Au mediator on top of the WO_3 . The impact of a site control for electron reaction is evident when comparing our results with earlier works.^[14] We show that proper placement and stacking of the TiO_2 - WO_3 -Au structure leads to a significantly higher photocatalytic efficiency than any individual combination, and can lead to a $\sim 100\%$ increase of H_2 evolution rate compared to a classic Au- TiO_2 configuration.

2. Results and Discussion

In the present work the photocatalytic platform is based on a highly-ordered anodic TiO_2 NT array scaffold. The TiO_2 NTs are grown on Ti foils by anodization in a hot $\text{H}_3\text{PO}_4/\text{HF}$

electrolyte.^[21] **Figure 1a** shows that these NTs have a high degree of ordering with hexagonal packing, and each NT has an individual inner diameter of ~ 100 nm and a depth of ~ 200 nm. These short and defined nanotubes can be easily site-selectively decorated at their top (tube rim) with metal films using a grazing angle sputtering technique.

An example of the resulting structures is illustrated in Figure 1b-d. This structure is formed by sputter-coating a W metal layer (nominal thickness $\sim 10\pm 0.3$ nm) on the top of the TiO₂ NTs. The deposition of the W film atop the NTs is homogeneous (Figure 1b) as evident from the narrowing of the NT inner diameter (from ~ 100 nm to ~ 60 -80 nm). Then, a thin layer of Au (1 ± 0.1 nm-thick) is sputtered over the W metal coating atop the NTs (see Inset in Figure 1c). Afterwards the structures are thermally treated in air at 450°C (1h).

It is evident from Figure 1c,d that the thermal treatment leads to a conversion of the thin Au film into Au NPs of spherical shape, with an average diameter of 4-8 nm, that are homogeneously decorated at the WO₃ interlayer.

The formation of Au NPs upon annealing is caused by solid state dewetting of the noble metal film.^[22-24] Thin Au films subjected to a temperature below the Au melting point split open and retract into distinct islands. Noteworthy, this process also exposes more of the substrate underneath.

We used Au cocatalyst not only to prove the principle, but also since thermal dewetting of Au (to form defined Au cocatalytic nanoparticles) is less critical than for other metals, owing to its lower melting point, better inertness and surface mobility of Au atoms.^[22,25]

The structures in Figure 1a-d were characterized by XRD and XPS in view of their composition. The results are compiled in Figure 1e,f. While as-formed TiO₂ NTs are amorphous, annealed structures are converted into an anatase-rutile mixed phase. The intense XRD peaks at $2\theta = 25.3^\circ$ and 27.5° can be assigned to TiO₂ (101) anatase and (110) rutile reflections, respectively. The XPS survey shows that the annealed structures are mainly composed of Ti, O, W and Au, with traces of (adventitious) carbon. The XRD peaks at $2\theta =$

44.5° and 64.7° can be assigned to Au (200) and (220) reflections.^[26] The XPS doublet with signals peaking at ~ 84.9 and 88.7 eV is well in line with Au4f B.E. values reported in the literature,^[21] and confirms the metallic state of the dewetted Au nanoparticles. The XRD peaks at $2\theta = 23\text{--}24^\circ$ (Figure 1e) and the XPS doublet peaking at ~ 36.5 and 38.7 eV can be attributed to formation of monoclinic WO₃ phase^[27,28] – thus, while the Au films undergo dewetting into NPs, the thin W film reacts with O₂ gas during the thermal treatment in air and forms a crystalline WO₃ interlayer.^[29]

The amount of sputtered metal and sequence can be adjusted to fabricate different morphologies. Structures formed by varying the amount of sputter-coated Au are illustrated in **Figure S1**. The SEM images in Figure S1a-d are of TiO₂ NTs that were coated with a 1 nm-thick W film, followed by deposition of Au layers of various thicknesses (1-10 nm) and by a suitable heat treatment. It is evident that the thicker the Au sputter-coated film, the larger the dewetted individual Au NPs and the wider the particle spacing. Au films with nominal thickness of 1 ± 0.1 , 2 ± 0.1 , 5 ± 0.2 and 10 ± 0.3 nm lead upon dewetting to spherical Au NPs that are 6, 7, 14 and 16 nm-sized, respectively (Figure S1e). This is in line with theory on solid state dewetting, that is, it is commonly observed on ideally flat substrates that the thicker the metal film, the larger the dewetted nanoparticles, the larger their interspacing and the broader their size distribution.^[22,25,30–33]

Figure 2 illustrates the morphology and Ti and W surface content of structures fabricated by depositing on the NTs various amounts of W (0-20 nm) prior to Au (1 nm), followed by a suitable heat treatment. The SEM images in Figure 2a-d show that W films ≥ 5 nm result in a clearly visible WO₃ layer that conformally coats the TiO₂ NT top. **Figure S2** show the XPS sputter profile results for a sample coated with 5 nm of W and then 1 nm of Au (i.e. 1Au-5WO₃-TiO₂). These data clarify the distribution of the different elements on the TiO₂ nanotube structures – that is, both Au and W are mainly placed at the nanotube opening.

The XPS data in Figure 2e provide evidence that with increasing the amount of sputter-coated W metal, the W surface content (i.e. the thickness of the WO₃ interlayer) increases, while the TiO₂ signal (attributed to the TiO₂ NT substrate) gradually vanishes – in other words, when a ~ 20 nm-thick W film is coated on the NTs, the TiO₂ surface is almost fully coated by the formed WO₃. In general, for large amounts of sputter-coated W, the WO₃ film is formed not only at the tube top but also deep in the TiO₂ cavities (leaving behind no free TiO₂ surface). A side result of the amount of sputter-coated W is that while for small amounts of W the tube opening is relatively wide and may allow to some extent for access/transport of Au in the nanotubes, large amounts of sputter-coated W may partially block the access offering a larger top surface where Au can be deposited.

An example of a structure obtained by decorating the NTs with ~ 1 nm-thick W and Au films is shown in **Figure 3a-c**. The SEM and TEM images in Figure 3a,b show that, upon dewetting, the sputtered Au film forms Au nanoparticles at the NT rims (*i.e.*, at the top of the NT walls). The WO₃ interlayer is not clearly visible (and distinguishable from TiO₂ and from the Au NPs) although its presence is confirmed by the XPS data in Figure 2e (with a W surface content ~ 4 at%). Thus, in this case it is expected that the formed WO₃ interlayer is as thin as a few nm.

A clearer analysis of the structure is provided by the HR-TEM image in Figure 3c, in which both the crystalline WO₃ interlayer and the dewetted Au NPs can be clearly identified at the top of the TiO₂ NT rims. The observed lattice fringes with crystal plane distances of 3.51, 3.35 and 2.35 Å are well in line with those reported in the literature for (101) anatase TiO₂, (120) monoclinic WO₃ and (111) Au crystallographic planes, respectively.^[26,27,34] The Au decorations have a spherical shape and an average diameter of 6 nm (smaller Au NPs are also present that are ~ 2-3 nm-sized).

The different Au-WO₃-TiO₂ structures were assessed in view of their photocatalytic H₂ generation ability from water-ethanol mixtures under UV light irradiation. The results are compiled in Figure 3d,e.

The data in Figure 3d show that pristine TiO₂ NTs (*TiO₂*) show a negligible photocatalytic H₂ generation ($r_{H_2} \sim 0.02 \mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}$). The modification of TiO₂ NTs with WO₃ (*WO₃-TiO₂*) leads to virtually no change of r_{H_2} ($r_{H_2} \sim 0.03 \mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}$). As expected, when Au (1 nm) is sputter-coated and dewetted on the TiO₂ NTs (*IAu-TiO₂*), the H₂ generation rate is significantly improved up to $2.6 \mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}$. This is ascribed to the formation of Au/TiO₂ Schottky junction at the TiO₂ NT top where the co-catalytic Au NPs act as electron-trap and can facilitate charge separation and CB electron transfer to the environment – this decreases the probability of electron-hole recombination in TiO₂.^[35,36]

Remarkably, NTs modified at their top with both WO₃ and Au in minimal amounts (*IAu-WO₃-TiO₂*) lead to the highest H₂ generation rate, that is of $\sim 5.1 \mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}$, which corresponds to a $\sim 100\%$ improvement of the r_{H_2} compared to a classic noble metal-TiO₂ configuration (i.e. *IAu-TiO₂*). This can be explained in light of the photocatalyst structure, as sketched in Figure 3f: WO₃ is present at the NT top in the form of a few nm-thick interlayer, which carries at its surface the dewetted Au NPs. The formed TiO₂-WO₃ junction is beneficial for charge separation owing to a favorable band alignment. WO₃ CB lies below TiO₂ CB band as illustrated in Scheme S1. Thus, electrons generated in TiO₂ upon UV light absorption can be transferred to WO₃.^[37,38] As the WO₃ interlayer is only a few nm thick and is in intimate contact with the Au NPs, a further transfer (cascade type) of electrons from WO₃ to Au NPs (“electron sink”) occurs. In the final step, electron transfer to the environment for H₂ generation takes place – i.e., WO₃ acts as an electron buffer layer that mediates the cascade transfer rates by providing a suitable band alignment and thickness for extracting electrons from TiO₂ at specific rates, limiting “charge jam” at the TiO₂/WO₃ interface and thus electron-hole recombination in TiO₂.

The data in Figure 3e demonstrate that the sequence of W and Au sputter-deposition and thermal treatment strongly affects the photocatalytic H₂ evolution. We found that it is crucial to form the stacked Au-WO₃-TiO₂ structure as illustrated in Figure 3f, that is, the highest r_{H_2} is obtained when W is sputtered onto the TiO₂ nanotubes prior to Au. Moreover, the thermal treatment (that leads to WO₃ formation and Au dewetting) must be carried out after metal (W and Au) sputter-deposition. If annealing is carried out before Au deposition, dewetting of Au is prevented – TiO₂ nanotubes decorated with non-dewetted (*i.e.* conformal) Au films (*1W-anneal-1Au*) show significantly lower r_{H_2} ($\sim 2.5 \mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}$), probably owing to the undefined morphology of the Au co-catalytic particles and to a limited light absorption by TiO₂ (shading effects by the conformal Au coating). A single annealing step (*1W-1Au-anneal*) is advantageous compared to multiple thermal treatments carried out after each metal deposition step (*e.g.* *1W-anneal-1Au-anneal* leads to $\sim 1.0 \mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}$) – the reason for this is that the photocatalytic activity of TiO₂ NTs subjected to multiple annealing steps in O₂-containing atmosphere is negatively affected by the formation of large amount of rutile phase at the oxide/metal substrate interface and in the NT walls (the latter leads also to a partial collapse of the NT structure).^[25,32] If W is sputter-coated after Au, we either observed that Au dewetting is hindered (for relatively large amount of sputter-deposited W – in this case the W film acts as capping layer),^[29] or that Au dewetting occurs in a disordered fashion (*1Au-1W-anneal*). In any case, the poor photocatalytic activity of these structures (*e.g.* *1Au-1W-anneal* leads to $\sim 2.3 \mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}$) $\mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}/\text{TiO}_2$ interface at the top of the NTs.

To clarify the origin of the enhanced photocatalytic activity of the stacked Au-WO₃-TiO₂ triad we measure the photo-electrochemical and optical properties of different structures, along with their (“open circuit”) photocatalytic H₂ evolution performance under different illumination conditions – data are compiled in **Figure S2**, **Figure S4** and **Figure S5**.

The photocurrent spectra Figure S3a show that pristine TiO₂ nanotubes deliver the highest photocurrent in the UV range. On the contrary, structures modified with WO₃ and Au show a slightly improved photocurrent density in the 400-700 nm range (Figure S3b,c).

The photocatalytic H₂ evolution rate of sample 1Au-1WO₃-TiO₂ can also be measured under AM 1.5 simulated solar light irradiation (Figure S4) but is entirely caused by the UV component of the solar light – note that no H₂ is evolved if a 420 nm cutoff filter is applied. In addition, we observed that light absorption features of TiO₂ structures with and without WO₃ top layer are virtually identical at the wavelength used for the photocatalytic experiments (325 nm) – this is due to the low absorption by minimal amount of coated WO₃ (W film thickness ~ 1 nm). Corresponding reflectance spectra are shown in Figure S5.

These results therefore exclude that the higher photo-activity of Au-WO₃-TiO₂ architectures is caused by a different photon harvesting ability of the WO₃ layer or is due to a plasmonic enhancement.

In order to assess the impact on the photocatalytic efficiency of the Au/WO₃/TiO₂ interface, we explored by electrochemical impedance spectroscopy (EIS) the charge carrier kinetics of different structures both in the dark and under UV light irradiation.

EIS measurements for pristine TiO₂ nanotube layers are available in the supporting information. The data in **Figure S6**, i.e. Bode (Figure S6a,b) and Nyquist (Figure S6c) plots, show the presence of two time constants in the case of pristine TiO₂ NTs, which can be attributed to electrochemical double layer and space charge layer in the semiconductor – see the SI for a more complete discussion.

The equivalent circuit models used for data fitting along with the EIS results (Bode plots) of Au- and WO₃-modified TiO₂ NT structures are shown in **Figure 4a,b** and Figure 4c-f, respectively. With the EIS data in Figure 4c-f we focus particularly on the high frequency time constant, i.e. on the charge carrier kinetics in the space charge region (data in Figure 4e,f are also shown in full frequency range in **Figure S7**, both in the dark and under UV light

illumination). From the data in Figure 4c one can observe that an additional time constant becomes evident at higher frequencies for WO₃-coated NTs (*I*WO₃-TiO₂) under light irradiation. Such a time constant implies the occurrence of an additional capacitive element due to the space charge layer at the TiO₂/WO₃ interlayer – in other words, it is a measure for electron accumulation under light irradiation (and in the absence of Au) in the WO₃ layer^[37,38] – noteworthy, this element is absent for pristine TiO₂ NTs (see also Figure S6 and data in Table S1).

In the presence of Au the situation is different. When Au nanoparticles are placed at the top of the WO₃-coated TiO₂ structures the additional capacitive element observed for *I*WO₃-TiO₂ is no longer present. Also, the Au NPs lead to a lower overall impedance and cause a shift towards higher frequencies of the phase angle peak associated to the space charge region. These findings are in line with a fast charge (electron) extraction by the noble metal NPs, which prevents accumulation in the TiO₂ semiconductor and in the WO₃ buffer layer. In summary, the EIS data confirm that the WO₃ interlayer acts as a mediating trap for TiO₂ CB electrons, and thus is a key element for the remarkable H₂ evolution improvement observed for the Au-WO₃-TiO₂ structures under UV light irradiation.

We also explored the photocatalytic performance of planar (flat) Au-WO₃-TiO₂ photocatalysts – see the H₂ evolution data in **Figure S8**. The highest r_{H_2} was measured for flat oxides decorated with only a 1 nm-thick Au layer, while layers sputter-coated with both W and Au exhibit a dramatically lower photocatalytic efficiency. The reason for this poor photocatalytic activity is that the sequential deposition of 1 nm-thick W and Au films over the “flat” TiO₂ layers leads almost to a full coverage of the TiO₂ surface and thus no free TiO₂ surface (exposed to the reaction phase) is left behind. For these structures the probability of charge recombination is probably higher (compared to NT structures) due to a hindered transfer of TiO₂ hole to the electrolyte.^[39]

By contrast, the TiO₂ nanotube structure owing to its defined geometry and short aspect-ratio allows for site selective Au and WO₃ decoration of only the NT top. This can enable two photocatalytically active zones. The H₂ evolution is confined mainly at the NT rims due to the presence of the Au/WO₃/TiO₂ double junction that efficiently drives electrons towards the environment. The situation for holes is different: owing to the natural upward bending of TiO₂ bands in the nanotube walls^[40] (the walls are < 10 nm-thick), and considering also the short diffusion length of holes in TiO₂, the most plausible fate for holes generated deep in the TiO₂ structure is a facilitated transfer to the electrolyte (where oxidation of hole-scavenger molecules takes place) allowed by free TiO₂ surface directly exposed to the reaction phase. This interpretation is confirmed by the remarkable effect that the amounts of deposited WO₃ and Au have on the photocatalytic efficiency of the NT structures, as illustrated in **Figure 5**. The r_{H_2} data in Figure 5a show that while a thickness of the sputter-coated Au film of 1 nm is an optimized condition, significantly lower H₂ evolution rates are obtained with larger Au loadings. This must be ascribed to the morphology of the Au NPs dewetted on the WO₃-coated TiO₂ nanotubes. Dewetting of Au films > 2 nm leads to larger Au NPs and higher decoration density compared to 1 nm-thick Au films (Figure S1). This may result in a TiO₂ shading effect, *i.e.*, TiO₂ is exposed to a lower photon flux and less charge carriers are generated.

Concerning the amount of WO₃, while a nominal W thickness of 1 nm (or more generally < 5 nm) leads to maximized H₂ generation rates (Figure 5b), the photo-activity was found to decrease when increasing the amount of formed WO₃. In line with the EIS data, this result is ascribed to the thickness of the formed WO₃ interlayer, that is, a thin WO₃ film (few nm) is able to trap TiO₂ CB electrons and leads to their efficient transfer to the Au NPs via a fast-kinetic electron transfer cascade. On the other hand, the electron transfer across WO₃ becomes slower for WO₃ interlayers formed from W films > 5 nm owing to a higher charge

transfer resistance. In addition, large amounts of WO_3 limit the free TiO_2 surface exposed to the environment (Figure 2e) causing a less efficient hole scavenging.

3. Conclusion

The present work introduces the fabrication of a photocatalyst for H_2 generation based on site-selective modification of TiO_2 nanotube arrays with WO_3 charge-separation and Au charge-transfer cocatalysts. We used a metal sputter-deposition/dewetting approach that together with the geometry of the TiO_2 nanotube substrate is key to the formation of a defined $\text{Au}/\text{WO}_3/\text{TiO}_2$ interface at the NT top. In contrast to previous studies based on $\text{Au}-\text{WO}_3-\text{TiO}_2$ composites synthesized by powder technology approaches, this architecture shows H_2 evolution rates higher than those measured for a classic $\text{Au}-\text{TiO}_2$ configuration owing to a geometrically defined electron transfer cascade. For constructing this functional architecture, crucial are the thickness of the WO_3 buffer layer and size/density of the dewetted Au nanoparticles atop the nanotubes, which were adjusted with nanoscale precision to achieve fast electron separation-transfer kinetics. In the ideal photocatalyst design, the bottom of the NT cavity is left uncoated (free TiO_2 surface) and allows for facilitated hole scavenging. From a more general point of view, tools such as self-ordering anodization, site-selective sputter-deposition of thin metal films and thermal dewetting/oxidation allowed us to demonstrate that a high level of control of the cocatalyst/photocatalyst stacking as well as the cocatalyst placement can enable advanced functionalities such as a fast and directional electron transport-transfer, thereby impacting dramatically on the overall photocatalytic efficiency.

4. Experimental Section

Fabrication of the TiO_2 Nanotube Arrays:

Ti foils (Advent Research Materials, 0.125 mm thickness, 99.6+% purity) were polished in a mixture of HF, HNO₃ and H₂O (1:4:2 vol%) for 10 s followed by washing with deionized (DI) water. Then, the Ti foils were anodized in a hot H₃PO₄ electrolyte containing 3 M HF, at 15 V for 2 h using a DC power supply (VLP 2403 Voltcraft). Ti metal was used as working electrode and a Pt sheet was used as counter electrode. After anodization, the TiO₂ nanotube arrays on Ti metal substrates were rinsed with ethanol and dried under N₂ stream. Compact (flat) anodic TiO₂ layers were fabricated as reference materials from Ti foils (pre-treated as outlined above) by anodization in aqueous 0.5 M H₂SO₄ electrolyte, at an applied voltage of 20 V for 30 min. After anodization, the compact TiO₂ layers were rinsed in DI water and dried in a N₂ stream.

W and Au Sputtering-Coating:

In order to form the WO₃ layer and Au nanoparticles on the TiO₂ nanotube arrays, a plasma-sputtering machine (EM SCD 500, Leica) was used to sputter-coat W and Au metal thin films. The applied sputtering current was 16 mA and the pressure of the sputtering chamber was set at 10⁻² mbar of Ar. The amount of sputtered material was *in situ* determined by an automated quartz crystal monitor, and is reported in this work as nominal thickness of the sputtered film. Subsequently, the samples were annealed at 450°C in air for 1 h, using a Rapid Thermal Annealer (Jipelec Jetfirst 100 RTA), with a heating and cooling rate of 30°C min⁻¹.

Characterization of the Structures:

Field-emission scanning electron microscope (FE-SEM, Hitachi S4800) and high resolution transmission electron microscope (HR-TEM, Philips CM300) were used to characterize the morphology of the samples. The chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5600, US). X-ray diffraction (XRD) with a X'pert

Philips MPD (equipped with a Panalytical X'celerator detector) was employed to examine the crystallographic properties of the materials.

The light absorption properties (UV-Vis diffuse reflectance) of the different structures were measured by a UV-Vis Spectrometer (Lambda 950, Perkin Elmer).

Photocatalytic Measurements:

For the photocatalytic H₂ generation experiments, the different TiO₂ structures on Ti foil were welded to a Ti wire. Then, the samples were immersed into a 20 vol% ethanol-water solution within a quartz tube that was used as photocatalytic reactor (ethanol was used as hole-scavenger). Before sealing the quartz tube with a gas-tight cap, the Ti wire was stuck into the bottom side of the cap, in order to hold and immobilize the tube layers within the photocatalytic reactor. The ethanol-water solution (volume = 7 mL, kept under static conditions during the runs) and the cell head-space (volume = 8 mL) were purged with N₂ gas for 30 min prior to photocatalysis. The light source used for the photocatalytic experiments was a HeCd laser with emission $\lambda = 325$ nm, and an emission intensity of 40 mW cm⁻² (Kimmon, Japan). The laser beam was expanded to a circle-shaped light spot of 1 cm in diameter, thus illuminating a sample surface of ~ 0.78 cm². In order to determine the amount of H₂ generated under irradiation, the composition of the gas accumulated in the headspace of the quartz reactor was analyzed by gas chromatography (using a GCMS-QO2010SE chromatograph, Shimadzu). The GC was equipped with a thermal conductivity detector (TCD), a Restek micropacked Shin Carbon ST column (2 m x 0.53 mm) and a Zebron capillary column ZB05 MS (30 m x 0.25 mm). GC measurements were carried out at a temperature of the oven of 45°C (isothermal conditions), with the temperature of the injector set to 280°C and the TCD fixed to 260°C. The flow rate of the carrier gas, *i.e.*, argon, was 14.3 mL min⁻¹.

In general the experiments lasted 5 hours and the amount of evolved H_2 was measured at the end of the experiments.

Photocatalytic experiments were also carried out under AM 1.5 (100 mW cm^{-2}) simulated solar light irradiation, using a 300 W Xe lamp solar simulator (with optical filter, Solarlight RT). In some cases, a 420 nm cutoff filter was applied. The photocatalytic experiments carried out under simulated solar light irradiation lasted 24 h.

Photo-electrochemical Measurements:

The photo-electrochemical properties of the different structures were evaluated using a classical three-electrode set-up in 0.1 M Na_2SO_4 with the NT layers on the Ti metal substrates as working electrode, a platinum plate as counter electrode and a Ag/AgCl (3 M KCl) electrode as a reference electrode, and using an Oriel 6365 150 W Xe lamp equipped with an Oriel Cornerstone 7400 1/8 m monochromator. The applied bias was + 500 mV.

Electrochemical Impedance Spectroscopy (EIS):

EIS measurements for the different TiO_2 structures were performed at OCP in a frequency range of 30 kHz to 100 mHz and with a peak-to-peak amplitude of the AC signal of 10 mV using a Zahner IM6 (Zahner Elektrik, Kronach, Germany) with a tunable TLS03 UV (369 nm) light source. The photoelectrochemical performance of the samples was analyzed in aqueous 0.2 M H_2SO_4 solution in a three-electrode configuration. The TiO_2 NT layers (nominal active area of 1 cm^2) were used as photo-anode. A platinum wire was used as counter electrode. An Ag/AgCl (3 M KCl) electrode was adopted as reference. The EIS spectra were fitted by EC-Lab software and randomize plus Levenberg-Marquardt method was employed.

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Figure 1. (a-d) SEM images of various TiO_2 structures: (a) arrays of pristine anodic TiO_2 nanotubes. Inset: cross-sectional view of the pristine NTs; (b) TiO_2 NTs coated with a sputtered 10 ± 0.3 nm-thick W film; (c) top and (d) cross-sectional views of TiO_2 NTs sequentially coated with W (10 ± 0.3 nm-thick) and Au (1 ± 0.1 nm-thick) films and then annealed at 450°C (air, 1 h). Inset in (c): top view of the Au-W-coated TiO_2 NT structure before thermal treatment (dewetting), showing that the as-deposited Au film appears as a conformal layer coating structure. (e) XRD patterns of various TiO_2 NT structures. The XRD pattern of as-formed (*i.e.*, amorphous) TiO_2 NTs shows only the typical XRD reflections of the Ti substrate. Inset: magnified view of the XRD patterns showing the main reflections of anatase and rutile TiO_2 , monoclinic WO_3 , and Au. (f) XPS survey of sample $1\text{Au}-10\text{WO}_3-\text{TiO}_2$ and high resolution XPS spectra of the Au4f and W4f regions.

Figure 2. (a-d) Top view SEM images of TiO₂ NTs sputter-coated with W films of various thicknesses (0-20 nm) and then with a 1±0.1 nm-thick Au film. The structures were subjected to annealing in air at 450°C (1 h). (e) Ti and W surface content (determined from XPS analysis) as a function of the nominal thickness of the sputter-coated W films.

Figure 3. (a) SEM and (b,c) TEM images of sample $1Au-1WO_3-TiO_2$. The HR-TEM image (c) shows crystal planes of (101) anatase TiO_2 , (120) monoclinic WO_3 and (111) Au. (d,e) Photocatalytic H_2 evolution results of different TiO_2 nanotube structures: (d) summary of the r_{H_2} improvement achieved with an optimized Au and WO_3 decoration on the top of the TiO_2 NT arrays; (e) r_{H_2} data as a function of the different metal sputter-deposition and annealing sequences. (f) Sketch outlining the structure of sample $1Au-1WO_3-TiO_2$ and illustrating the proposed mechanism of charge transfer for the photocatalytic evolution of H_2 . Sample $1Au-1WO_3-TiO_2$ is fabricated by sequential sputter-coating of 1 nm-thick W and Au layers atop the TiO_2 NT arrays, followed by annealing at $450^\circ C$ (air, 1 h). The NTs result decorated at their top with a few nm-thick WO_3 interlayer that carries ca. 6 nm-sized spherical Au NPs. The magnified view of the sketch shows the top of the NTs. The WO_3 layer mediates the electron transfer from TiO_2 to the Au NPs and then onward to the environment for H_2 generation. TiO_2 holes diffuse towards the oxide/environment interface and react with ethanol to form CO_2 . The H_2 generation and ethanol oxidation reactions are confined at the top and bottom of the NT cavities, respectively.

Figure 4. (a,b) Equivalent circuit models used for EIS data fitting. The circuits (a) and (b) were used for pristine and WO_3 -coated TiO_2 NTs under UV light irradiation, respectively. (c-f) EIS results (Bode plots) of pristine TiO_2 NTs, and of Au- and WO_3 -modified TiO_2 NT structures under 369 nm light irradiation.

Figure 5. Photocatalytic H₂ evolution results of different TiO₂ nanotube structures as a function of (a) Au and (b) W sputtered amount.