Site-Selective Pt Dewetting on WO₃-Coated TiO₂ Nanotube Arrays: an Electron Transfer Cascade-Based H₂ Evolution Photocatalyst

by Davide Spanu^{a,b}, Sandro Recchia^b, Patrik Schmuki^{a,c,*}, Marco Altomare^{a,*}

^a Department of Materials Science and Engineering WW4-LKO, University of Erlangen-Nuremberg, Martensstrasse 7, D-91058 Erlangen, Germany.

^b Department of Science and High Technology, University of Insubria, via Valleggio 11, 22100 Como, Italy

^c Chemistry Department, Faculty of Sciences, King Abdulaziz University, 80203 Jeddah, Saudi Arabia Kingdom

* Corresponding authors. Email: schmuki@ww.uni-erlangen.de (Patrik Schmuki)
marco.altomare@fau.de (Marco Altomare)

link to the published article:

<https://www.sciencedirect.com/science/article/abs/pii/S0926337318304910>

Abstract

Here we introduce a highly defined charge separation platform for photocatalytic H₂ evolution based on a Pt-WO₃-TiO₂ “stacked” structure constructed on TiO₂ nanotube arrays. Key is the formation of a site-selective sequential W and Pt metal sputter-decoration only on the mouth of highly-ordered TiO₂ nanotubes. Then a thermal treatment forms a WO₃ layer while the Pt film undergoes self-ordered dewetting into 2-6 nm-sized Pt nanoparticles. These structures show strongly improved photocatalytic H₂ evolution efficiency compared to any other one-cocatalyst system (i.e. Pt-TiO₂ and WO₃-TiO₂) and pristine TiO₂ nanotubes. This significant improvement is ascribed to an enhanced charge carrier separation enabled by the well-defined TiO₂-WO₃-Pt cascade that provides swift charge carrier separation and transfer towards H₂ evolution.

Keywords: Anodic TiO₂ nanotube arrays; Pt dewetting; WO₃; photocatalytic H₂ generation; charge separation and transfer

1. Introduction

Since the pioneering work of Fujishima and Honda [1] in 1972, the production of H_2 by photocatalytic splitting of H_2O on semiconductors has been extensively investigated. Among the different studied photocatalysts, titanium dioxide (TiO_2) received large attention owing to its suitable conduction and valence band edge positions, as well as for its nontoxicity and stability against corrosion and photo-corrosion [2,3]. The bottom of TiO_2 conduction band (CB) lies higher than the redox potential of water (-0.45 and 0 V vs. NHE, respectively, at pH 0) [4]. Therefore, by promoting electrons in TiO_2 CB through UV light irradiation ($E_g TiO_2 \sim 3.0\text{-}3.2$ eV), it is possible to reduce H_2O to H_2 .

However, pristine TiO_2 shows low efficiencies for H_2 production – even under UV light because of trapping and recombination of charge carriers, and owing to a kinetically slow electron transfer to reactants. Nanostructured photocatalysts can be employed in order to improve the electron transfer efficiency. Particularly, one-dimensional (1D) nanostructures, such as anodic TiO_2 nanotubes (NTs), have attracted great attention in the last decades [5–7]. Entirely aligned arrays of self-organized NTs can be grown by a simple anodization of Ti metal in a suitable electrolyte [2,3,8]. The electrochemical conditions can be adjusted in order to lead to a large palette of nanotubular morphologies [8,9]. These highly-ordered 1D TiO_2 structures can promote directional charge transport and orthogonal electron-hole separation that allow for enhanced photo-electrochemical and photocatalytic performances [3,10].

In addition, cocatalysts that aid charge separation and transfer by forming a heterojunction on TiO_2 , such as a suitable semiconductor or noble metal nanoparticles (e.g. Au, Pd, Pt) can be also employed to further improve the performance of titania-based photocatalysts.

In view of constructing a composite photocatalyst, a particularly interesting constellation is obtained when TiO_2 is combined to WO_3 , an n-type semiconductor with a band gap $E_g WO_3 \sim$

2.6-2.8 eV [11,12]. With such a combination, a favorable band alignment at the TiO₂-WO₃ interface is generated that enables efficient charge separation [13] by transfer of TiO₂ CB electrons into the WO₃ CB [14–17]. Additionally a contribution to visible-light absorption by WO₃ ($\lambda_{\text{abs WO}_3} < \sim 450 \text{ nm}$) can lead to improved photon harvesting for TiO₂-WO₃ systems [18,19]. Other reported features achieved by combining Ti and W oxides are an enhanced surface acidity that can yield improved adsorption of reactants [20–25], and a higher hydrophilicity of Ti-W oxides [26].

While the placement of a suitable metal oxide semiconductor (WO₃) at the TiO₂ surface can enhance charge-separation, localized Schottky-type junctions are also commonly formed by placing noble metal cocatalytic nanoparticles on the individual oxides. For example, Pt is typically a most efficient cocatalyst for the H₂ generation reaction [27–30]. Pt nanoparticles at the TiO₂ surface can enable efficient electron transfer at the catalyst/environment interface by providing a favorable solid state junction to TiO₂ [4], hence improving the electron transfer to reactants while additionally catalyzing hydrogen atom recombination reaction, and thus facilitating H₂ gas formation ($2\text{H}^0 \rightarrow \text{H}_2$) [31,32].

These two cocatalyst principles, i.e. a charge separation cocatalyst (WO₃) and a charge transfer cocatalyst (Pt), can, based on an anticipated synergistic effect, be combined into a single composite photocatalyst, e.g. in a TiO₂-WO₃-noble metal combination.

Some recent studies, such as the work of Pap et al., investigated the photocatalytic performance of TiO₂-WO₃-noble metal (Au, Pt) powders [33–36]. These works point out the potential of combining the two cocatalyst principles, but the chosen photocatalyst preparation method, based on a powder technology process, was shown inadequate to achieve high control over morphology and stacking of the cocatalysts. Particularly, only a loose and undefined contact (junction) between the two oxides is by classical approaches obtained – this hampers

the charge carrier separation: note in fact that in these works any noble metal-WO₃-TiO₂ combination was found less photocatalytically active for H₂ evolution than a simple noble metal-TiO₂ configuration.

In contrast, with the present work, we introduce a reliable fabrication strategy of a synergistic Pt-WO₃-TiO₂ photocatalyst for H₂ generation constructed with nanoscale precision on an array of highly-ordered TiO₂ nanotubes. This architecture, owing to its highly-defined geometry, due to the site-selective placement of Pt and WO₃ cocatalysts, induces an electron transfer cascade from the TiO₂ NTs (light absorber) to the WO₃ junction (charge separation cocatalyst) and onward to the Pt nanoparticles (NPs) (charge transfer cocatalyst). The result is a facilitated electron transport towards the nanotube top for H₂ evolution, while the uncoated bottom of the TiO₂ cavities is a suitable site for hole-mediated oxidation reaction. We show that, in contrast to previous works based on powder technology approaches, a morphologically controlled TiO₂-WO₃-Pt design leads to enhanced photocatalytic efficiencies, which are higher than those measured for classic noble metal-TiO₂ photocatalysts.

2. Experimental

2.1. *Fabrication of the TiO₂ nanocavity array*

Ti foils (Advent Research Materials, 0.125 mm thickness, 99.6+% purity) were degreased by sonicating in acetone, ethanol, and deionized water, and were then dried in a N₂ stream. Then, the Ti foils were anodized to fabricate the highly ordered TiO₂ nanotube arrays in a hot electrolyte based on 3 M HF in o-H₃PO₄ (Sigma- Aldrich) [37]. For the anodic growth, a two-electrode configuration was used, where the Ti foil (15 mm × 15 mm) and a Pt sheet were the working and counter electrodes, respectively. The anodization experiments were carried out by applying a potential of 15 V (for 2 h) using a DC power supply (VLP 2403 Voltcraft). After

anodization, the TiO₂ nanotube arrays on Ti metal substrates were rinsed with ethanol and dried under N₂ stream.

2.2. *W and Pt sputtering-coating and thermal treatment*

In order to form the WO₃ layer and Pt nanoparticles on the TiO₂ nanotube arrays, a plasma-sputtering machine (EM SCD 500, Leica) was used to sputter-coat W and Pt metal thin films using a 99,8% pure W target (Hauner Metallische Werkstoffe) and a 99,99% pure Pt target (Hauner Metallische Werkstoffe), respectively. 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.

2.3. *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 an 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 (diffuse reflectance) of the samples were measured by a UV-Vis Spectrometer (Lambda 950, Perkin Elmer).

2.4. *Photocatalytic measurements*

Photocatalytic measurements for H₂ generation were carried out by irradiating the oxide films with UV light (LED Opsytec, $\lambda = 365$ nm, beam size = 0.785 cm², power of 80 mW cm⁻²).

²) in a 20 vol% ethanol–water solution (ethanol was used as hole-scavenger) in a quartz tube sealed with a gas-tight cap. The ethanol-water solution (kept under static conditions during the runs) and the cell head-space (volume = 6.22 mL) were purged with N₂ gas for 15 min prior to photocatalysis.

N₂-purging is strictly needed as O₂ would reduce the efficiency of H₂ generation by competitive photocatalytic reduction to O₂^{•-} (O₂ can react with conduction band electrons).

The amount of produced H₂ (which was accumulated over the irradiation time in the head space of the tube) was measured by using a gas chromatograph (GCMSQO2010SE, Shimadzu) equipped with a thermal conductivity detector and a Restek micropacked Shin Carbon ST column (2 m × 0.53 mm). GC measurements were carried out at a temperature of the oven of 45 °C (isothermal conditions), with the temperature of the injector set at 280 °C and that of the TCD fixed at 260 °C. The flow rate of the carrier gas, i.e., argon, was 14.3 mL min⁻¹. All the experiments lasted 5 hours and the amount of evolved H₂ was measured at the end of the experiments. Photocatalytic measurements of Acid Orange 7 (AO7) degradation were carried out with the same instrumental setup and using a 0.125 mM AO7 solution. The light absorbance of the solution was measured by using a UV-Vis spectrophotometer (Lambda XLS+, Perkin Elmer) at 485 nm wavelength (maximum absorbance value) in order to determine the AO7 concentration.

3. Results and discussion

Fig. 1a shows the morphology of the highly-ordered anodic TiO₂ NTs used in this work, which are grown on Ti metal foils by anodization in a hot H₃PO₄/HF electrolyte [37]. These NTs have an almost ideal hexagonal packing, an average inner diameter of ~ 80-90 nm and a length of ~ 190-200 nm (see Inset in Fig. 1a).

This well-defined structure with short aspect-ratio allows for the site-selective decoration of only the NT top, with e.g. metal films (Pt and W in this work) using a grazing-angle sputtering technique.

After the sputter-deposition of the metal film, a thermal treatment is carried out to crystallize the TiO₂ NTs. Worth nothing, as illustrated in Fig. 1b, such a thermal treatment leads also to self-ordered solid state dewetting of Pt, that is, to the conversion of the sputtered Pt film into single spherical Pt nanoparticles with an average diameter of 2-6 nm (as shown in Fig. 1c and d). The driving force for solid state dewetting [38] is the minimization of the free surface energy of the metal film, of the substrate and of the metal-substrate interface. Since the thinner the metal film the higher its surface-to-volume ratio and thus its surface energy, the dewetting of e.g. few nm-thick metal films can occur also at temperature far below the metal melting point - that is, the film can dewet while remaining in the solid state [39].

The NT structures can also be decorated by sputtering a W film firstly (nominal thickness of 0-30 nm), followed by sputter-deposition of a thin Pt metal layer (nominal thickness of 1 nm) - i.e. using a sequential metal sputter-coating approach. A subsequent thermal treatment of these structures in air at 450 °C for 1 hour forms the architectures illustrated in Fig. 2 (additional SEM images of similar structures are reported in Fig. S1).

In the case of small amounts of shallow-angle sputtered W (nominal thickness < 10 nm, e.g. Fig. 2a and b), it is possible to observe from the cross-sectional SEM picture (Fig. 2b) that the deposition of the W film occurs only at the rim of the tubes, thus leaving the tube bottom uncovered (free TiO₂ surface). However, for thicker W films (≥ 10 nm, Fig. 2c and d) a certain amount of W is deposited also deeper in the NTs – e.g. Fig. 2d shows that WO₃ is formed also close to the NT bottom.

The structures in Fig. 1 and 2 were characterized by XRD, HR-TEM and XPS in view of their composition and structure. The results are compiled in Fig. 3. The intense XRD peaks (Fig. 3a) at $2\theta = 25.4^\circ$ and 27.6° can be assigned to TiO_2 (101) anatase and (110) rutile reflections, respectively, while peaks at $2\theta \sim 23\text{-}24^\circ$ can be ascribed to the monoclinic WO_3 phase. The relatively intense reflections at $2\theta \sim 23\text{-}24^\circ$ observed for the structure 1Pt-30 WO_3 - TiO_2 is well in line with the larger amount of sputtered W metal (additional XRD patterns are shown in Fig. S2). In any case, no XRD signal for Pt can be seen, probably owing to the little amount of sputtered noble metal.

The TEM images in Fig. 3b clearly show the decoration of the top of the tubes with the two cocatalyst (i.e. Pt and WO_3). The HR-TEM images (insets in Fig. 3b) reveal the presence of both anatase TiO_2 (101) and rutile TiO_2 (110) in the sidewalls and bottoms of the tubes, and, confirm the site-selective placement of the monoclinic WO_3 layer and Pt NPs on the top of the tubes.

The XPS surveys (Fig. S3a) show that the structures are composed of Ti, O, W and Pt, with small traces of adventitious carbon and P (due to the anodization in highly-concentrated o- H_3PO_4). The XPS doublet with signals peaking at ~ 71.3 and 74.7 eV (Fig. S3b) can be assigned to $\text{Pt}4f_{7/2}$ and $\text{Pt}4f_{5/2}$, respectively [40], and confirms the metallic state of the dewetted Pt nanoparticles. The XPS doublet peaking at ~ 36.5 and 38.7 eV (Fig. S3c) can be attributed to WO_3 [41,42]. Note that in contrast to what is observed for Pt (i.e. solid-state thermal dewetting leading to rupture of the Pt film into Pt NPs), the sputter-coated W film is subjected to a different fate when annealed in air: it reacts with O_2 gas and forms a crystalline WO_3 layer atop the NTs [43].

The XPS data reported in Fig. 3c show that the $\text{Ti}2p$ signal for the NT structures decreases with increasing the amount of sputtered W. This is well in line with data in Fig. S3d, and

indicates that the WO₃ layers formed from W sputtered films > 10 nm cover almost totally the TiO₂ NT surface. The weak Ti signal is in this case attributed to the uncovered TiO₂ surface at the very bottom of the tubes. A side effect of sputter-coating W film > 5 nm is the increase of the surface content of Pt at the top of the structures. This can be ascribed to the narrowing of the tube mouth (as clearly shown in Fig. 2c and d). Hence, the relatively large amount of deposited W makes available a larger surface on the top of the cavities for Pt deposition.

The XPS depth profiling (Fig. 3d) further corroborates the stacked architecture of the photocatalyst, with the presence of Pt and WO₃ only at the very top of the tubes, i.e. the signals of Pt and W decrease sharply from the NT top towards the bottom of the cavities.

These structures were assessed in view of their photocatalytic H₂ evolution performance, from water-ethanol (20%) solution under UV light irradiation (LED light, 365 nm). The results are shown in Fig. 4a-c. From these data it is clear that, for these stacked structures, an optimized amount of sputtered W leads to significantly higher photocatalytic H₂ generation efficiency than any other combination (Pt-TiO₂, WO₃-TiO₂ and pristine TiO₂). More precisely, both pristine TiO₂ NTs (TiO₂) and TiO₂ NTs modified only with WO₃ (3WO₃-TiO₂) exhibit a negligible photocatalytic H₂ generation (0.06 $\mu\text{L h}^{-1} \text{cm}^{-2}$ and 0.14 $\mu\text{L h}^{-1} \text{cm}^{-2}$, respectively). The slight improvement of the r_{H_2} may be ascribed to electron-hole separation at the TiO₂/WO₃ interface, which can make electrons more available for the H₂ evolution. As expected, Pt-TiO₂ photocatalyst (1Pt-TiO₂) shows an improved H₂ evolution compared to pristine TiO₂, i.e. leading to a r_{H_2} of 3.4 $\mu\text{L h}^{-1} \text{cm}^{-2}$. This effect is due to the formation of Pt/TiO₂ Schottky junctions at the TiO₂ nanotubes top.

Nevertheless, a substantial further enhancement of the photocatalytic performance is obtained modifying TiO₂ with both WO₃ and Pt (1Pt-xWO₃-TiO₂), that is, by constructing a stacked Pt-WO₃-TiO₂ architecture at the NT top. In particular, photocatalysts with 1, 3 and 5

nm of WO₃ lead to the highest H₂ generation rates, that is, of 4.4, 5.0 and 5.2 $\mu\text{L h}^{-1} \text{ cm}^{-2}$, respectively. Note that these r_{H_2} can be up to a factor 1.5 higher than that of 1Pt-TiO₂. Long-run photocatalytic tests (Fig. 4c) reveal that the r_{H_2} does not change also after several hours of irradiation. Thus, deterioration phenomena, such as photo-corrosion of the photocatalyst or fall-off of the cocatalytic Pt NPs can be ruled out.

Taking into account the band edge alignment and energetic situation of the elements of the Pt-WO₃-TiO₂ triad, one can interpret these photocatalytic results assuming that the defined Pt-WO₃-TiO₂ architecture constructed at the top of the NT walls enables efficient electron transfer from the TiO₂ NTs (light absorber and charge carrier generator) to the WO₃ top layer, and then onward to the Pt cocatalytic NPs. This “electron transfer cascade” is therefore the main cause for the observed synergistic r_{H_2} enhancement. A side effect of the site-selective decoration of the NT top only (W films < 10 nm) is that the bottom of the TiO₂ nanocavities is left uncoated, i.e. free TiO₂ surface. This situation, along with the intrinsic upward band bending in the nanotube walls [44] and the typically short diffusion length of holes in TiO₂, leads to direct hole-transfer to the reactants (ethanol), this reducing the electron-hole recombination in the NTs.

In order to corroborate the results of photocatalytic H₂ evolution and their interpretation, photo-degradation tests of Acid Orange 7 (AO7) under 365 nm UV light irradiation were carried out with the reference material 1Pt-TiO₂ and different three-layered structures, i.e., 1Pt-3WO₃-TiO₂ and 1Pt-30WO₃-TiO₂. The results are reported in Fig. 4d and e. Noteworthy, also in this case the Pt-WO₃-TiO₂ triad with optimized amount of W (~1-5 nm) leads to a faster photocatalytic performance (AO7 degradation) compared to 1Pt-TiO₂. However, a too large amount of W (~30 nm) leads to a lower AO7 degradation rate. In other words, these data mirror the H₂ evolution results.

In order to understand the role of the thickness of the WO_3 top layer, the light absorption properties of the different structures were investigated by measuring their UV-Vis diffuse reflectance (DR-UV-Vis) spectra (see Fig. 5). Interestingly, only minor differences in terms of light absorbance between the various morphologies were observed at 365 nm. Considering these results, it is clear that the light harvesting ability of the different structures (i.e. different W loadings) does not have a dominant effect on the photocatalytic performance.

Thus, one can assume that the Pt- WO_3 - TiO_2 structure is properly constructed only when the WO_3 top layer is sufficiently thin: in this case it can favor charge carrier separation by electron transfer towards the top of the tube, through the WO_3 buffer layer, and then onward to the Pt NPs for H_2 evolution (as illustrated in Fig. 6). In this construction, crucial is also the naked bottom of the TiO_2 cavities that allows for direct hole-transfer to the reaction phase (hole-scavenging). This proposed mechanism explains also the low H_2 yield of the sample 1Pt-30 WO_3 - TiO_2 , that is, a too thick WO_3 buffer layer not only blocks TiO_2 hole-transfer to the environment at the tube bottom, but also can make the electron transport across the WO_3 layer less efficient owing to an increased charge transfer resistance (this is well in line with EIS results obtained for similar stacked-architectures [13]).

4. Conclusions

We introduced the fabrication of an efficient photocatalytic platform based on an electron transfer cascade mechanism designed by site-selective decoration of the top of highly-ordered TiO_2 nanotubes with a well-defined WO_3 -Pt cocatalyst stack. In contrast to previous work, we show that a morphological control with nanoscale precision of the cocatalyst-catalyst architecture, is the key requirement in order to achieve strongly enhanced photocatalytic H_2 evolution efficiencies in such cascade structures.

Acknowledgements

The authors would like to acknowledge ERC, DFG and the DFG cluster of excellence EAM for financial support, as well as H. Hildebrand, S. Hejazi, and N.T. Nguyen for valuable technical help.

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Figure Captions

Fig. 1

(a-f) SEM images of various TiO_2 structures: (a) arrays of pristine TiO_2 nanotubes. Inset: cross-sectional view of the pristine NTs; (b) TiO_2 NTs coated with a sputtered 1 nm-thick Pt film after dewetting (thermal treatment at 450°C , air, 1h). Inset: cross sectional view. (c) TEM image of the very top of a nanotube decorated with a sputtered-dewetted 1 nm-thick Pt film; (d) Pt NPs size distribution.

Fig. 2

(a, c) Top and (b, d) cross sectional views of TiO_2 NTs coated with (a, b) 5 nm-thick and (c, d) 30 nm-thick W film and then with Pt (1 nm-thick) film after thermal treatment.

Fig. 3

(a) Magnified view of the XRD patterns showing the main reflections of anatase and rutile TiO_2 , monoclinic WO_3 , and Pt (XRD patterns measured in the $20\text{--}80^\circ 2\theta$ range are in Fig. S2). (b) TEM images of sample 1Pt-5 WO_3 - TiO_2 . Insets: HR-TEM images: (yellow) crystal planes of (101) anatase TiO_2 and (110) rutile TiO_2 in the sidewalls and bottom of the nanotubes; (blue) crystal planes of (002) monoclinic WO_3 and (red) crystal planes of (111) cubic Pt at the very top of the nanotubes. (c,d) Ti, W and Pt surface content determined from XPS analysis: (c) surface content as a function of the nominal thickness of the sputter-coated W films and (d) depth profile (content measured along the depth of the nanotubes).

Fig. 4

(a) Photocatalytic H₂ evolution results of different TiO₂ nanotube structures as a function of W sputtered amount; (b) summary of the r_{H_2} improvement achieved with an optimized Pt and WO₃ decoration on the top of the TiO₂ NT arrays. (c) Evaluation of the photocatalytic H₂ evolution performance of 1Pt-3WO₃-TiO₂ over an irradiation time of 30 h. (d) First-order kinetic fitting for the photocatalytic degradation (oxidation) of AO7 (Acid Orange 7) using different TiO₂ nanotube structures. (e) AO7 degradation rates for the different samples.

Fig. 5

Detail of the DR-UV-Vis spectra of different TiO₂ structures in the region around 365 nm (i.e. wavelength used in this work for the photocatalytic experiments). Inset: DR-UV-Vis spectra measured in the 200-800 nm wavelength range.

Fig. 6

Scheme of the structure of the three-layered photocatalyst illustrating the band alignment (TiO₂-WO₃ [45] energetic situation) that allows for the proposed mechanism of electron transfer cascade.

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6