Anodic TiO₂ Nanotube Membranes: Site-Selective Pt-Activation and Photocatalytic H₂ Evolution

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Abstract

Anodic TiO₂ nanotube membranes of various thicknesses (1.5-60 μm) fixed on FTO slides were site-selectively decorated with Pt nanoparticles at only their upper extremity. Their photocatalytic H₂ evolution ability (with and without Pt) is investigated under UV light (325 nm) illumination through the FTO slide. The irradiation side is opposite to the Pt decorations in order to avoid Pt shading effects. This design is key to study the H₂ evolution in relation to membrane thickness, light absorbance, and electron diffusion length in the nanotubes. The Pt decoration improves the H₂ evolution, and the photocatalytic enhancement, quantified as ratio of H₂ evolution rate with Pt vs. that without Pt, varies with the membrane thickness. The highest photocatalytic enhancement is for 5-10 μm -long nanotubes, owing to maximized photon harvesting and efficient electron trapping/transfer to reactants. This is enabled by a short pathway of electron diffusion towards Pt. The photocatalytic enhancement drops dramatically for membrane > 30 μm while membranes of intermediate lengths (~ 10-30 μm) show similar photocatalytic enhancement. This can be ascribed to an electron diffusion length in Pt-TiO₂ nanotubes of 20-30 μm .

Keywords: anodic TiO₂ nanotube membranes • Pt dewetting • photocatalytic H₂ evolution • electron diffusion length • light absorbance

Introduction

Since the pioneering work of Fujishima [1], TiO_2 has been widely investigated as photocatalyst for various environmental applications, such as the degradation of organic pollutant in air and wastewater, and particularly for the generation of H_2 via water splitting [2,3]. Upon absorption of UV photons ($\lambda < \sim 400 \text{ nm}$), electrons that are photo-promoted to the conduction band (CB) of TiO_2 are able to reduce water to H_2 . However, the H_2 generation efficiency of pristine TiO_2 is typically low, owing to slow kinetics of electron transfer to the environment and to intrinsic electron-hole recombination.

An effective strategy to overcome these limitations is the use of nanostructured TiO_2 . In TiO_2 nanostructures the photo-generated charge carriers have to diffuse over short distances (few nm or few tens nm) before reaching the reactants at the photocatalyst/environment interface. This aids improving the photocatalytic efficiency by reducing the probability of electron-hole recombination in TiO_2 .

TiO_2 nanotubes (NTs) became in the last decades a most widely investigated photocatalytic material, owing to their one-dimensional morphology that provides orthogonal charge separation and direct electron percolation pathway [4]. These nanotubes can be fabricated by electrochemical anodization of Ti metal under self-organizing conditions. A key advantage of this approach is that simple electrochemical parameters (e.g. electrolyte temperature and composition, applied voltage etc.) can be controlled to adjust the nanotube morphology with nanoscale precision [5–7]. Furthermore, strategies were developed to detach anodic TiO_2 NT layers from the Ti metal substrate, thus obtaining “self-standing” TiO_2 NT membranes. Many efforts have been devoted to achieve a reliable lift-off of intact TiO_2 NT layers because the membranes can then be transferred onto a desired support, for example an optically transparent substrate such as FTO-coated glass, for further photocatalytic [8,9] and photo-electrochemical

(e.g. dye-sensitized solar cells) [10–12] applications. This configuration allows also for studying optical features of TiO₂ nanotube layers such as their light transmittance properties [13], which cannot be measured for conventional nanotube layers supported on Ti metal foils.

Besides nanostructuring, other approaches to achieve further enhancement of the photocatalytic performance can be (i) the addition to the reaction phase of an organic compound (e.g. methanol, ethanol etc.) that acts as scavenger for TiO₂ valence band (VB) holes, and (ii) the modification of TiO₂ surface with a charge transfer cocatalyst such as noble metal (Au, Pt, Pd) nanoparticles (NPs) [14,15]. For the H₂ generation reaction, Pt is a most efficient cocatalyst – Pt NPs provide a favorable solid state junction to TiO₂ that can improve the electron transfer kinetics at the photocatalyst/environment interface. In addition, Pt can also catalyze hydrogen atom recombination reaction, thus facilitating H₂ gas formation ($2\text{H}^0 \rightarrow \text{H}_2$) [16].

An example of photocatalytically efficient Pt-TiO₂ geometry was reported by Nguyen et al. [17]. In their work, cocatalytic Pt NPs are decorated only at the opening (mouth) of TiO₂ NT arrays. This architecture can induce a gradient of the semiconductor Fermi level (E_F) in the tube walls along the length of each NT, which can in turn facilitate the transfer of electrons generated deep in the TiO₂ NT structure towards the noble metal-TiO₂ coupled zone [18,19]. In other words, the geometry provides a light harvesting zone (UV light penetration depth in the tube structure can be ca. few 100 nm up to few μm for $\lambda \sim 325 \text{ nm}$ [13]) which generates photo-promoted electrons that can diffuse towards the Pt-TiO₂ charge-transfer zone (photocatalytically active tube top) for H₂ evolution [9].

In the present work, we fabricate 1.5 to 60 μm -thick TiO₂ nanotube membranes and transfer them onto FTO slides in an upside-down configuration (i.e. with the nanotube top side facing the FTO). The membranes are then decorated with Pt nanoparticles at the upper side only, by a

site-selective Pt sputter-dewetting approach. The thermal treatment used for inducing Pt dewetting leads simultaneously to crystallization of the NT membranes into anatase TiO₂.

We investigate the photocatalytic H₂ evolution ability of these structures (both in the presence and absence of Pt cocatalyst) under UV light illumination through the FTO substrate. The placement of Pt opposite to the irradiation side avoids Pt shading effects. This design is key to evaluate the photocatalytic results in relation to light absorbance, electron diffusion length and membrane thickness.

We found that the “photocatalytic enhancement”, a parameter quantified as the ratio of H₂ evolution rate with Pt vs. that without Pt, varies significantly as a function of the membrane thickness, suggesting that the photocatalytic performance is the result of a trade-off between light absorbance and electron diffusion length. A maximized photocatalytic enhancement is measured for nanotube length of 5-10 μm , owing to an efficient electron trapping/transfer kinetics. However, it is estimated that the electron diffusion length in Pt-TiO₂ nanotubes under “open circuit conditions” can be up to several tens of μm (e.g. 10-30 μm), and thus only for membrane thicker than $\sim 30 \mu\text{m}$ a significant drop of the H₂ evolution performance is observed, i.e. electrons can be harvested over a several 10 μm and can reach the Pt NPs (i.e. H₂ evolution site).

Experimental

Different approaches are reported in the literature to fabricate self-standing TiO₂ nanotube layers, such as mechanical detachment (peeling off by tape), potential shock, and chemical etching [20]. In the case of mechanical detachment, an adhesive material (tape, polymer) is applied to the TiO₂ nanotube layers and is used to apply mechanical force for its detachment. The detached TiO₂ nanotube layers have a close bottom end, and thus a subsequent step would

be necessary in order to obtain double side opening. Potential shock is based on e.g. a steep increase of the applied voltage at the end of the anodization. The voltage transition leads to gas evolution and local acidification of the electrolyte (which causes etching) that simultaneously lead to detachment of the TiO₂ nanotube layers from the Ti substrate and to the opening of the tube bottom ends. However, owing to the variation of the tube bottom morphology for nanotube layers of different thicknesses, this method could require parameter optimization for each desired membrane thickness. Chemical etching (outlined below in details) was chosen in this work as a most convenient and reliable approach since it leads to both the detachment of the nanotube layer and opening of the tube bottom end under the same optimized experimental conditions regardless of the membrane thickness.

For this, Ti sheets of a thickness of 0.125 mm and purity of 99.6 % (Advent Materials, UK) were used to grow the TiO₂ nanotube layers. The Ti sheets were cut into 1.6 cm x 1.6 cm pieces and were cleaned (before anodization) in an ultrasonic bath with acetone, ethanol, and distilled water (20 min in each solvent). After sonication, the Ti sheets were dried in a nitrogen stream.

TiO₂ nanotube layers were grown by electrochemical anodization in a glycol ethylene-based electrolyte containing 0.15 M NH₄F and 3 vol% H₂O (all reagents were provided by Sigma Aldrich). The electrochemical experiments were carried out in a two-electrode electrochemical O-ring cell, with the Ti foil and a Pt gauze being the working and the counter electrodes, respectively. The applied potential was provided by a LAB/SM 1300 DC power supply (ET System).

The thickness of the nanotube layers was adjusted by the anodization time. After anodization, the nanotube layers were rinsed with ethanol and dried in a N₂ stream. The lift-off procedure for the nanotube layers in order to obtain self-standing NT membranes is described in details in the section “Results and Discussion” (a summary is outlined in Fig. 1a). After lift-

off, the membranes were transferred upside-down onto FTO glasses that were previously coated by doctor blading a 2.5 μm -thick layer of TiO_2 NPs (TiO_2 Solaronix paste). The FTO slides were 2.5 cm x 1.5 cm x 0.2 cm and were provided by Solaronix.

After fixation on FTO, the NT membranes were sputter-coated at only the NT bottom with a thin Pt film (nominally 5 nm-thick) by Ar-plasma sputtering system (EM SCD500, Leica). A Pt target (99.99%, Hauner Metallische Werkstoffe) was used as Pt source. The pressure of the sputtering chamber was reduced to $\sim 10^{-4}$ mbar before initiating sputtering, and then set at $\sim 10^{-2}$ mbar of Ar during sputtering. The applied current was 16 mA. The amount of sputtered Pt, in terms of nominal thickness of the sputter-deposited Pt film, was determined in situ using an automated quartz crystal film-thickness sensor.

Afterwards, the membranes were exposed to a thermal treatment in air at 450°C, using a Rapid Thermal Annealer (Jipelec Jetfirst 100 RTA), with a heating and cooling rate of 30°C min^{-1} . The thermal treatment not only induced crystallization of the as-formed amorphous NT into anatase TiO_2 , but led also to solid-state thermal dewetting of the Pt film into Pt NPs.

For morphological characterization, a field-emission scanning electron microscope (Hitachi FE-SEM S4800) was used. The cross-sectional images were obtained by cracking the TiO_2 nanotube layers. X-ray diffraction analysis (XRD, X'pert Philips MPD with a Panalytical X'celerator detector) using graphite monochromized Cu $K\alpha$ radiation (wavelength 1.54056 Å) was used for determining the crystallographic composition of the samples. The measurements were carried out with the following parameters: step size 0.03°; time per step 2 s; scan rate (continuous) 0.015 ° s^{-1} . In the XRD patterns, the measured intensity [counts] is normalized vs. the time per step [s], and thus the intensity is plotted as [cps]. Chemical composition was determined by X-ray photoelectron spectroscopy (XPS, PHI 5600, US).

The light transmission measurements were carried out by irradiating the FTO-supported NT membranes with monochromatic UV laser light provided by 325 nm laser (IK3552R-G, KIMMON, $I_0 = 60$ mW). The intensity of the monochromatic light passing through the TiO_2 NT membranes was measured using a calibrated power meter 1830-C (Newport).

For photocatalytic H_2 generation experiments, the TiO_2 NT membranes (pristine or Pt-decorated) on FTO slides were attached to a Ti wire. Then, these samples were immersed into a 20 vol% methanol-water solution in a quartz tube that was used as a photocatalytic reactor (methanol was used as a hole scavenger). The addition of an organic (e.g. methanol, ethanol, etc.) to water for the photocatalytic experiments typically leads to significantly larger H_2 evolution rates [14]. The reason is that the organic molecules can be efficiently oxidized by valence band holes in TiO_2 . The consumption of holes reduces the possibility of charge recombination in TiO_2 . As a consequence, TiO_2 conduction band electrons have a longer lifetime and can more efficiently diffuse towards the TiO_2 surface where they react with the environment. The methanol-water solution and the cell headspace (volume = 6.8 mL) were purged with N_2 gas for 20 min prior to photocatalysis (in order to remove O_2). Before sealing the quartz tube with a gastight cap, the Ti wire was stuck into the bottom side of such a cap, in order to hold and immobilize the sample within the photocatalytic reactor. The light source used for the photocatalytic experiments was the same HeCd laser used for the transmittance measurements. The laser beam was expanded to a circle-shaped light spot of 1 cm in diameter, thus illuminating a sample surface of 0.785 cm^2 .

In order to determine the amount of H_2 photocatalytically generated under UV light irradiation, the composition of the headspace of the quartz reactor was analyzed by gas chromatography (using a GCMS-QO2010SE chromatograph, Shimadzu). Gas samples (200 mL) were withdrawn at regular times during irradiation, using a gas-tight syringe, and were

directly injected into the GC. The GC was equipped with a thermal conductivity detector (TCD), a Restek micropacked Shin Carbon ST column ($2\text{ m} \times 0.53\text{ mm}$), and a Zebron capillary column ZB05 MS ($30\text{ m} \times 0.25\text{ mm}$). 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} . All the experiments lasted 7 h, and the amount of evolved H_2 was measured after 5 and 7 h for the pristine TiO_2 NT membranes, and after 1, 3, 5 and 7 h for the Pt-decorated TiO_2 NT membranes.

Results and Discussion

The sketch in Fig. 1a illustrates the process for fabricating FTO-supported TiO_2 NT membranes. In order to improve the self-ordering degree of the NTs, the first step is anodizing the Ti foil to grow a $10\text{ }\mu\text{m}$ -thick TiO_2 NT layer that is then removed from the Ti substrate by sonication in water. The removal leaves behind hexagonally-ordered dimples at the surface of the Ti metal substrates, which act as preferential initiation sites for the subsequent anodic growth [21,22]. The second anodization step (different durations) is to grow NT layers of desired thickness in the $1.5\text{-}60\text{ }\mu\text{m}$ range. These NT arrays are then annealed in air at 250°C for 2h – this leads to a partial crystallization of the NTs. The structures are then subjected to a third anodization step that forms an underneath NT layer of $\sim 4\text{ }\mu\text{m}$.

At this point the upper NT layer is lifted-off by immersing the sample for 3 h in an aqueous H_2O_2 solution at room temperature that leads to preferential etching of the underneath amorphous $\sim 4\text{ }\mu\text{m}$ -thick NT layer – the upper NT layer can survive the etching treatment without undergoing any structural deterioration owing to its partial crystallinity. The result is self-standing bottom-opened TiO_2 NT membranes.

After lift-off, the membranes are soaked in methanol and are then directly transferred in a bottom-up-configuration onto the TiO₂ NP-coated FTO slides. A cross-sectional SEM image of an example of this architecture is shown in Fig. 1b – in this case the TiO₂ NT membrane is ~ 28 μm -thick.

The optical image in Fig. 1c shows FTO-supported membranes of different thicknesses (1.5-60 μm). In the as-formed state, these membranes are colored, that is, the membranes interfere with visible light, and the thicker the membrane the darker the color. This can be ascribed to the intrinsic carbon content of as-formed anodic nanotube layers owing to uptake of carbon species during the anodization in the organic-based electrolyte. Nevertheless, the structures turn clear (white, Fig. 1d) when annealed at 450°C (this step is discussed below) owing to burn-off of the carbon content [13].

The fabricated membranes were characterized in view of their morphology and physicochemical properties by SEM, XRD and XPS.

The cross-sectional SEM images in Fig. 2 show that our fabrication approach provides fine control over the NT membrane thickness. Remarkably, membranes as thin as e.g. 1.7 and 2.8 μm can be fabricated (shown in Fig. 2a,b). From Fig. 2 one can observe that NT layers > 20 μm show a “grassy” structure of the NT top. This is because the NT layers are exposed for long time to the F-containing electrolyte and undergo etching of the tube top, causing a partial collapse of their tubular structure [23]. In the used architecture the NT top is in contact to the FTO substrate (bottom-up configuration).

As shown in Fig. 3, the gap between adjacent tubes at the tube bottom is not substantially affected by the anodization time: these cross-sectional SEM images show the bottom morphology of tubes in the case of ca. 5 μm (Fig. 3a-c) and ca. 30 μm -thick Pt-decorated membranes (Fig. 3d-f). One can see that the gap between adjacent tubes is in any case of

maximum 20 nm, and that the Pt penetration depth is always 100-200 nm regardless of the tube length. The images also show that the tube diameter measured close to the tube bottom slightly increases with increasing the anodization time: e.g. the outer diameter is ~ 120 and 150 nm for (Fig. 3c) ~ 4.3 and (Fig. 3f) 28.0 μm -thick tubes.

The planar SEM images in Fig. 4a-d show the typical structure of the bottom of a TiO_2 NT membrane before (Fig. 4a,b) and after Pt NP decoration (Fig. 4c,d). Clearly, the lift-off strategy leads to a uniform opening of the tube bottom with a 100% success rate.

The site-selective decoration of the membrane bottom with Pt NPs is obtained by a simple Pt sputtering-dewetting approach [18,24–26]. The membranes are firstly sputter-coated with a 5 nm-thick Pt film. Then the structures undergo a suitable thermal treatment in air at 450°C that leads to dewetting of Pt, that is, the noble metal film retracts and splits open [27], forming 5-30 nm-sized Pt NPs. The agglomeration of Pt also partially exposes the underneath TiO_2 surface.

The cross-sectional SEM images in Fig. 4e-f clarify the morphological evolution of the sputtered Pt film that takes place with annealing. The as-sputtered Pt film coats homogeneously the very bottom of the NTs (Fig. 4e). The site-selective placement of the Pt film (at only the NT extremity) is due to the morphology of the NT bottom (narrow tube opening) and, particularly, to the use of a shallow sputtering angle. The thermal treatment leads to a clear agglomeration of the noble metal film into NPs (Fig. 4f,g).

The results of XRD and XPS analysis of these structures are compiled in Fig. 5. The XRD patterns in Fig. 5a show that, regardless of the thickness, all the membranes undergo crystallization into pure anatase TiO_2 upon annealing in air at 450°C (1 h) – this is evident from the intense signal at 25.6° assigned to the main reflection of (101) anatase TiO_2 . The signals of the FTO substrates also appear, and are indicated with the symbol “*”. In addition, the data in Fig. 5b confirm that the as-formed membranes are amorphous. The relatively weak (101)

anatase signal is a sign a poor crystallinity resulting from the low temperature annealing (250°C, 2 h, air) performed prior to the third anodization. Moreover, the presence of crystalline Pt decorations on membranes subjected to Pt sputter-dewetting is confirmed by the intense signal at 39.8° assigned to the (111) reflection of cubic Pt phase (inset in Fig. 5b).

The XPS survey spectra (Fig. 5c) taken for different membranes at the NT bottom show that the structures are composed of Ti, O, and Pt (the latter is present only in the case of Pt-decorated membranes), with small traces of adventitious carbon and nitrogen. The XPS doublet (Fig. 5d), observed for the Pt-decorated membrane, with signals peaking at ~71.3 and 74.5 eV can be assigned to Pt4f_{7/2} and Pt4f_{5/2} [28], respectively, this confirming the metallic state of the dewetted Pt nanoparticles.

The FTO-supported TiO₂ NT membranes, both pristine and Pt-decorated, were investigated in view of their photocatalytic H₂ evolution performance. The results are compiled in Fig. 6a,b.

A first observation is that for all the structures the amount of evolved H₂ increased linearly over time. We can thus exclude photocatalytic deactivation phenomena ascribed to e.g. structural deterioration (membrane detachment etc.). The photocatalytic performance can be discussed in terms of (constant) H₂ evolution rate r_{H_2} expressed in $\mu\text{L}_{H_2} \text{ h}^{-1} \text{ cm}^{-2}$.

Secondly, the r_{H_2} varies as a function of the membrane thickness (both with and without Pt).

Thirdly, the presence of Pt NPs leads to a strong increase of the photocatalytic performance. This is ascribed to the formation of a suitable Schottky junction at the TiO₂ surface that aids trapping TiO₂ CB electrons and their transfer to the environment. In other words, as expected, the Pt NPs act as a cocatalyst that enables a faster kinetics for transfer of electrons to reactants through the TiO₂/Pt/environment interface for H₂ evolution. The Pt NPs additionally induce a localized harvesting center for electrons generated in the underneath nanotubes.

In order to clarify the effects of Pt-decoration and membrane thickness on the photocatalytic performance, we found it useful to compile the photocatalytic results in term of r_{H_2} as shown in Fig. 6c. Evidently, a most optimized range of membrane thickness in view of a maximized H_2 evolution rate is 5-10 μm , for both pristine and Pt-decorated NTs. Thinner ($< 5 \mu\text{m}$) and thicker ($> 15 \mu\text{m}$) NT membranes lead to a lower photocatalytic efficiency. Nevertheless, the r_{H_2} for pristine membranes varies significantly less as a function of the membrane thickness (between $0.45\text{-}1 \mu\text{L}_{\text{H}_2} \text{h}^{-1} \text{cm}^{-2}$) than for Pt-TiO₂ structures (between $30\text{-}70 \mu\text{L}_{\text{H}_2} \text{h}^{-1} \text{cm}^{-2}$).

The trend of r_{H_2} vs. membrane thickness for pristine TiO₂ structures can be explained in terms of optimized light absorption. Fig. 7a shows the light transmittance as a function of membrane thickness. An increase of the NT length up to $\sim 10 \mu\text{m}$ leads to a decrease of transmitted light ($\lambda = 325 \text{ nm}$) [13]. This means that NT membranes $< 5 \mu\text{m}$ do not absorb all the irradiated photons and lead thus to a suboptimum r_{H_2} . On the contrary, 5-10 μm -thick membranes grant a full light absorption and hence outperform thinner structures.

In principle, thick membranes ($> 10 \mu\text{m}$) can also grant a maximized photon harvesting. However, in the absence of Pt charge transfer cocatalyst, it is expected that the electron transfer (at the oxide/environment interface) and the H_2 evolution reaction do not take place at a specific site, but occurs close to the light harvesting zone – electrons diffuse along the TiO₂ by “random-walk” since there is no driving force to “pull” them along a defined pathway (electron trapping by Pt NPs). Owing to the irradiation configuration, the UV photons are absorbed in the portion of the NT membrane that is close to the FTO substrate. Thus, for thick NT membranes, the charge carriers are generated far away from the opening to the reaction phase – this may limit the photocatalytic activity owing to diffusion limits and evolved H_2 gas blockage.

The situation for Pt-decorated membranes is different. Taking into account the relatively low r_{H_2} observed for pristine structures $> 30 \mu\text{m}$ and given their dramatic r_{H_2} enhancement obtained

by Pt decoration, one can assume that in Pt-TiO₂ NTs photo-promoted electrons can diffuse within the NT walls towards Pt where a comparably fast H₂ evolution reaction takes place. This induces a directional diffusion gradient within the tube walls [19] close to the Pt decoration that additionally aids directional electron transport.

The presence of Pt NPs leads to virtually identical light transmittance for all the structures regardless of their thickness (Fig. 7a), although pristine membranes < 10 μm are not thick enough to grant full photon harvesting. It is thus plausible that for these layers, Pt may induce some back-scattering or back-reflection effects [29].

The H₂ generation results illustrated in Fig. 6c can be examined in terms of “photocatalytic enhancement factor”, calculated as the ratio of the H₂ evolution rate with Pt vs. that measured without Pt. The enhancement factor is plotted in Fig. 7b along with light transmittance data as a function of the membrane thickness.

The trend of the enhancement factor and light absorbance vs. membrane thickness suggests that since the H₂ evolution reaction is confined at the Pt-TiO₂ coupled zone, the overall photocatalytic performance is the result of a trade-off between light harvesting, average electron diffusion length and distance between the charge carrier generation zone and the H₂ evolution site (Pt NPs), and is therefore directly related to the membrane thickness.

One can thus conclude that:

- For membranes < 5 μm the distance between the charge carrier generation zone and the Pt NPs is minimized (charge carriers can be generated at any depth in the membrane). Thus, photo-promoted electrons have to diffuse over short distances (few 100 nm or few μm) towards the Pt NPs, and are subjected to a relatively low probability of charge recombination. Nevertheless, these membranes are too thin to grant full light absorption.

- A thickness range of 5-10 μm is a most optimized condition that leads to the highest r_{H_2} and photocatalytic enhancement. This results from a full light harvesting, along with a tube length that matches the electron diffusion length.
- For 10-30 μm -thick membranes, although light is fully absorbed, the charge carriers are generated several μm away from the Pt NPs and electrons may be subjected to higher probability of recombination. However, the photocatalytic enhancement factor is almost constant, suggesting that electron diffusion length in TiO_2 NTs (under our experimental conditions) is of some 30 μm [30].
- For membranes $> 30 \mu\text{m}$ the electron-withdrawal effect of Pt is minimized since the spatial separation between the light harvesting zone and reaction site exceeds the average electron diffusion length. This explains both the low r_{H_2} and photocatalytic enhancement factor.

Conclusions

We developed a reliable strategy to fabricate anodic TiO_2 nanotube membranes with thickness in the 1.7-60 μm range that were then fixed onto FTO slides and were photocatalytically activated for the H_2 evolution reaction by a Pt sputter-dewetting approach. These structures were investigated as H_2 evolution photocatalysts under 325 nm light irradiation through the FTO substrate. The photocatalyst design and light irradiation configuration, i.e. light illumination opposite to the Pt-decorated side, are crucial to interpret the photocatalytic performance in relation to light absorbance and electron diffusion length in the nanotubes. Key for this is the site-selective placement of Pt cocatalytic nanoparticles only at the nanotube end as well as a membrane fabrication strategy that allows for a fine-tuning of the membrane thickness.

Two distinct zones take action in the H₂ evolution reaction. The TiO₂ membrane absorbs light and generates charge carriers. The Pt-TiO₂ coupled zone is the catalytically active zone and enables a one-dimensional withdrawal pathway for TiO₂ conduction band electrons, facilitating their transfer to reactants. We showed that the overall photocatalytic performance not only is determined by the light harvesting ability of the nanotube structures, but is also related to the distance between the charge carrier generation zone and the H₂ evolution site, that is, to the electron diffusion length in the nanotubes. Based on our results, it is estimated that Pt decoration of the membranes can enable an electron pulling effect that leads to an electron diffusion length of up to some tens of μm .

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Figure Captions

Figure 1

(a) Sketch illustrating the steps for fabricating FTO-supported Pt-decorated TiO₂ nanotube membranes; (b) Cross-sectional SEM image illustrating a typical Pt-decorated TiO₂ nanotube membrane architecture and the 325 nm light irradiation configuration; (c,d) Optical images of FTO-supported TiO₂ nanotube membranes of different thicknesses (c) before and (d) after annealing in air at 450°C (1h).

Figure 2

Cross-sectional SEM images of TiO₂ nanotube membranes of different thicknesses.

Figure 3

Cross-sectional SEM images showing the bottom morphology of tubes in the case of 4.3 μm (a-c) and 28.0 μm -thick Pt-decorated membranes (d-f). The horizontal white arrows indicate the gap between adjacent tubes (< 20 nm) and the outer tube diameter. The vertical white arrows indicate the Pt penetration depth (~ 100 -200 nm) outside (a,d) and inside (b,e) the nanotubes.

Figure 4

(a-d) Top-view SEM images of the bottom of (a,b) pristine and (c,d) Pt-decorated TiO₂ nanotube membranes; (e-f) Cross-sectional SEM images of the bottom of TiO₂ nanotube membranes sputter-coated with a 5 nm-thick Pt film (e) before and (f,g) after thermal dewetting.

Figure 5

(a,b) XRD and (c,d) XPS data of different pristine and Pt-decorated TiO₂ nanotube membranes. Legend for (a,b): “A” anatase TiO₂, “Pt” platinum, “*” FTO.

Figure 6

(a,b) Amount of photocatalytically evolved H₂ measured over irradiation time for (a) pristine and (b) Pt-decorated TiO₂ nanotube membranes of different thicknesses; (c) Photocatalytic results expressed in terms of H₂ evolution rate (r_{H_2}) for pristine and Pt-decorated TiO₂ nanotube membranes plotted as a function of the membrane thickness.

Figure 7

(a) Light transmittance of pristine and Pt-decorated TiO₂ nanotube membranes of different thicknesses; (b) photocatalytic enhancement factor (i.e. ratio of r_{H_2} measured with Pt vs. that measured without Pt) and light transmittance plotted as a function of the membrane thickness.

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7