Effect of different hole scavengers on the photoelectrochemical properties and photocatalytic hydrogen evolution performance of pristine and Pt-decorated TiO₂ nanotubes

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Abstract

TiO₂ nanotubes have been investigated in photoelectrochemistry and photocatalysis for more than a decade. However, up to now, a systematic investigation of different hole scavengers is still lacking. Here we investigate the effect of the most relevant sacrificial hole scavengers on the photoelectrochemical properties and photocatalytic H₂ evolution performance of pristine and Pt-decorated anodic TiO₂ nanotubes. We examine methanol, isopropanol, ethylene glycol, EDTA-Na₂, as well as Na₂SO₃, and find that the incident photocurrent conversion efficiency (IPCE) of the TiO₂ nanotubes in 0.1 M Na₂SO₄ electrolytes increases by 1.8–3.1 times, depending on the used hole scavenger. The efficiency increases in the sequence Na₂SO₃ < isopropanol < MeOH < ethylene glycol < EDTA-Na₂. In presence of any hole scavenger, for nanotubes in the length-range of 2-10 μm, the photocurrent spectra and the ICPE magnitude are independent of the tube length. The photocurrent onset potential (optical flatband potential) is significantly affected by the different type of scavengers, in line with their red-ox potential. Under open circuit conditions (photocatalytic conditions), organic hole scavengers lead to a 10.0 - 28.8 times higher H₂ production by TiO₂ nanotubes than the scavenger-free case, with a sequence MeOH > i-PrOH > EDTA-Na₂ > EG, while a detrimental effect of Na₂SO₃ is observed. These results are compared to results obtained for TiO₂ particles, and discussed in terms of various concepts in the literature.

Keywords: TiO₂ nanotubes, hole scavengers, photoelectrochemistry, photocatalysis, H₂ generation

1. Introduction

Photocatalytic hydrogen (H_2) evolution is a prospective field of research due to the current high demand for environmentally friendly energy sources, the abundance of the solar light reaching the terrestrial surface, and the availability of photocatalytically active materials which can utilize the energy of absorbed radiation to reduce the protons present in water to H_2 . In this respect, titanium dioxide (TiO_2) has acquired wide attention from researchers, due to the high photocatalytic activity, outstanding photocorrosion resistance, nontoxicity, and economic viability of this material [1]. Nanotubular TiO_2 geometries are especially attractive for photocatalytic applications due to their high surface area combined with directionality to light and charge management [2]. TiO_2 nanotubes can be prepared by various methods, which can be roughly divided into templating, hydrothermal, and anodic self-organization approaches [3]. Using electrochemical anodization, almost ideal hexagonally arranged tube layers can be grown to a thickness of several hundreds of micrometers on Ti surfaces of virtually any shape. The formed TiO_2 nanotubes are directly electrically back-connected to the metal substrate [4]. The anodization process also allows for many variations in tube geometries and morphologies, including the formation of bamboo morphology, stacked tube layers, branched tubes, or transferable membranes [5].

One of the crucial factors limiting large-scale application of TiO_2 nanotubes for photocatalytic H_2 evolution is their low photonic efficiency, due to a rapid recombination of photogenerated electron-hole pairs [6]. Since the photocatalytic H_2 evolution reaction is driven by the photogenerated electrons, a fast removal of photogenerated holes from the photocatalyst is required to suppress recombination. A swift hole transfer to the electrolyte can be achieved by introduction of sacrificial hole scavengers to the reaction medium. A wide range of compounds have been investigated for TiO_2 nanopowders and particles, including various organics (alcohols [7–12], organic acids [8,10–13] etc.) and inorganics (S^{2-} , SO_3^{2-} [7,11,14–16], H_2S [14], I^-/IO_3^- [11,15], Ce^{3+} [15,17], Fe^{2+} [15] etc.). These species have a

suitable energetics for a direct hole capture from TiO₂ or for the reaction with intermediate •OH radicals. Hole capture causes the decomposition of organic molecules (via oxidation) or a change of the valence state of inorganic compounds ($I^{1-} \rightarrow I^{5+}$, $S^{2-} \rightarrow S^0$, $S^{4+} \rightarrow S^{6+}$, $Ce^{3+} \rightarrow Ce^{4+}$, $Fe^{2+} \rightarrow Fe^{3+}$ etc.). Therefore, unless conditions for a subsequent reduction of the oxidation reaction products are created (such as using I^-/IO_3^- , Ce^{4+}/Ce^{3+} or Fe^{3+}/Fe^{2+} redox pairs for mediating electron-hole transfer between two different photocatalysts [18]), a constant supply of new hole scavengers is required in order to maintain high H₂ evolution rates. While this requirement may seem to increase the cost of the produced H₂, many studies have shown that organic pollutants [19–23] and sulphides [24] present in industrial wastewaters, as well as plastic waste [25], can effectively be used as a sacrificial hole scavenger. This approach allows simultaneous H₂ evolution and water purification/photoreforming of plastic and other waste. Thus, the use of hole scavengers in H₂ generation may be economically and environmentally meaningful [7]. While various hole scavengers have been widely investigated for TiO₂ nanoparticle suspensions (see for example the overviews given in refs. [18,26,27]), a systematic comparison in the case of anodic TiO₂ nanotubes is entirely missing.

Here, we report and compare the effect of a range of selected organic and inorganic hole scavengers (methanol, isopropanol, ethylene glycol, EDTA-Na₂, sodium sulfite) on the photoelectrochemical properties of pristine TiO₂ nanotubes as well as their effect on the photocatalytic H₂ evolution from Pt-decorated TiO₂ nanotubes.

2. Experimental

2.1 Preparation of pristine and Pt-decorated TiO₂ nanotubes

TiO₂ nanotube layers of different thicknesses were formed by anodization of titanium foils. Prior to anodization, the foils (0.1 mm thick, 99.6% pure temper annealed, ADVENT) were cleaned by a sequential ultrasonic treatment in acetone, ethanol and deionized water (15 min in each liquid), followed by drying with nitrogen gas. The cleaned foils were anodized at room temperature in ethylene glycol containing 0.15 M NH₄F and 3 vol.% of deionized water at a constant voltage of 60 V for 0.5–30 min. For that purpose, a two-electrode electrochemical cell comprising of a Ti foil as an anode (anodization area of 0.785 cm²) and a platinum foil as a cathode (1.5 cm distance between electrodes) was utilized. Upon finishing the anodization process, the samples were washed with ethanol and dried with nitrogen gas. In order to crystallize the as-formed TiO₂ nanotubes, the samples were annealed in air at 450°C for 60 min. The as-annealed pristine TiO₂ nanotubes were then used in the photoelectrochemical studies.

For photocatalytic H₂ evolution experiments the TiO₂ nanotube samples were additionally decorated with Pt nanoparticles using a sputter coater with an Ar-plasma sputtering system (EM SCD500, Leica). The decoration was performed by sputtering a Pt target (99.99 %, Hauner MetallischeWerkstoffe) at Ar pressure of 10⁻² mbar (using a sputtering current of 15 mA), until a nominally 1 nm thick Pt film was deposited (according to an automated quartz crystal film-thickness sensor).

2.2 Morphological characterization

The morphology of the prepared samples was studied by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Philips CM30). The geometrical features were measured from SEM and TEM images using the Image J software.

The crystal structure of the tubular layers was analyzed by X-ray diffraction (XRD, X'pert Philips MPD with a Panalytical X'celerator detector) using graphite monochromized Cu K α radiation (wavelength 1.5406 Å). The approximate crystallite size was determined from the peak broadening of XRD reflections by the Scherrer formula [28] given in Eq. (1):

$$D = k\lambda/(\beta\cos\theta) \quad (1)$$

where D is the crystallite size, k is the Scherrer constant (0.9 in this study), λ is the wavelength of the X-ray radiation (0.15406 nm for Cu K α), and β is the full width at half-maximum (FWHM) in X-ray diffraction reflections of the anatase (101) and rutile (110) peaks of TiO₂.

The chemical composition of the Pt-decorated TiO₂ nanotubes was characterized with X-ray photoelectron spectroscopy (XPS, PHI 5600, USA) using monochromatic Al K α radiation (1486.6 eV, 300 W).

2.3 Photoelectrochemical and photocatalytic characterization

Photoelectrochemical measurements and photocatalytic H₂ evolution experiments were performed using aqueous electrolytes containing 0.1 M Na₂SO₄ and one of the following hole scavengers: 20 vol.% methanol (MeOH) (pH = 7), 20 vol.% isopropanol (i-PrOH) (pH = 7), 20 vol.% ethylene glycol (EG) (pH = 7), 0.1 M ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA-Na₂) (pH = 4) or 0.1 M sodium sulfite (Na₂SO₃) (pH = 8). A 0.1 M Na₂SO₄ solution without additives (pH = 7) was used as a reference.

The transient photocurrent response was studied by chopped light chronoamperometry using an Oriel 6365 150 W Xe-lamp equipped with an Oriel Cornerstone 7400 1/8 m monochromator as a light source and a three-electrode cell comprising of an Ag/AgCl (3 M

KCl) reference electrode, a Pt counter electrode and a TiO₂ nanotube sample as a working electrode. The current through the working electrode was recorded every 0.2 s, while it was irradiated by a monochromatic light in the wavelength range of 300 - 600 nm (with 5 nm steps) in the following sequence: light off (10 s); light on (20 s); light off (10 s). During the measurements a constant external voltage was applied between the working and the counter electrodes. The IPCE of the TiO₂ nanotubes was calculated at each wavelength using the Eq. (2) below:

$$\text{IPCE (\%)} = (I_{\text{ph}} \times h\nu / P \times \lambda) \times 100 \quad (2)$$

where I_{ph} is photocurrent density (mA cm⁻²), P is the power density of light (W cm⁻²), $h\nu$ is the photon energy of the incident light (≈ 1240 eV nm⁻¹), and λ is the wavelength of the light (nm).

Photocatalytic H₂ evolution by the Pt-decorated TiO₂ nanotubes was evaluated using an UV LED (90 mW, $\lambda_{\text{max}} = 365$ nm) as a light source. Each sample was fixed inside a quartz cell filled with the electrolyte, which was then purged with nitrogen gas for 20 min and sealed prior to irradiation. After 3 h of irradiation a 200 μ L sample of the gas atmosphere from the cell was taken and analyzed by a gas chromatograph (GCMS-QO2010SE, Shimadzu).

3. Results and discussion

Self-ordered layers composed of close-packed nanotubes were formed by anodization of Ti foils in an EG-based electrolyte. SEM images of the pristine TiO₂ nanotubes formed after 10 min of anodization are shown in Fig. 1a,b. With increasing the anodization time from 0.5 to 30 min, the length of the nanotubes increases from 0.55 ± 0.21 μ m to 10.88 ± 0.53 μ m (see Fig. S1 of the SI for the entire sequence of different length).

SEM images of the TiO₂ nanotubes (formed after 10 min of anodization) after Pt-decoration are shown in Fig. 1c. As can be seen from the images, the nominal deposition of 1 nm Pt leads to the formation of particulate films at the top of the tubes with the particle size of approx. 4.5 ± 2 nm.

Fig.1

All nanotube layers were crystallized by air annealing at 450°C. XRD patterns show a conversion of the tubes to anatase (Fig. 1d shows the XRD of the layers used in Fig 1a, b). XRD was also taken for Pt-decorated tubes (Fig 1c), which show the same diffraction peaks as the annealed pristine TiO₂ nanotubes. The approximate sizes of anatase crystallites calculated using Scherrer equation are 20.6 and 20.2 nm for pristine and Pt-decorated TiO₂ nanotubes, respectively. No diffraction peaks for Pt are observed, which indicates that the amount of Pt deposited by sputtering (nominal thickness of 1 nm) is below the detection limit of XRD.

A TEM image of a Pt nanoparticle on the TiO₂ nanotubes (10 min anodization) is shown in Fig. 1e. The TiO₂ nanotube wall shows crystalline lattice fringes, an example is given in Fig. 1f of a 0.355 nm distance, corresponding to (101) planes in anatase phase [29]. Additional identification of Pt in XPS is provided in the Fig. S2 of the SI.

In order to characterize the pristine crystallized tubes for their photoelectrochemical properties in presence and absence of hole scavengers, we acquired photocurrent spectra, photocurrent transients, and photocurrent voltage curves, as described in the experimental section. First we evaluated the influence of the TiO₂ nanotube length on the IPCE at an external voltage of 0.5 V vs. Ag/AgCl using a 0.1 M Na₂SO₄ solution as an electrolyte and in MeOH containing electrolyte (Fig. 2a). The IPCE spectra in both cases for the different TiO₂ nanotube layers were taken for irradiation wavelengths in the range of 300 - 600 nm. For

nanotubes in the sacrificial free electrolyte, the highest IPCE of 17.40 % (at the wavelength of 300 nm) is demonstrated by the 0.55 μm thick nanotube layer, which is closely followed by the 17.27 % IPCE (at the wavelength of 355 nm) for 4.58 μm long tubes. In the presence of MeOH, the highest IPCE of 43.34 % (at the wavelength of 350 nm) is observed for 4.58 μm thick nanotube layers (among the 2.19 - 10.88 μm thick nanotube layers). It is important to note that for the sacrificial capture free electrolyte, the IPCE maximum shifts to higher wavelengths with increasing the nanotube layer thickness, while for the MeOH containing electrolyte, the maximum remains independent of the tube length in the investigated range.

Fig.2

The observed IPCE maximum for thicker nanotube layers often is attributed to the wavelength dependence of the absorption coefficient of TiO_2 versus the carrier diffusion length [30,31], as illustrated in Fig. 3.

Fig.3

Consequently, a larger thickness of the material is required in order to completely absorb the light of longer wavelength. If the absorption is incomplete in the whole studied wavelength range due to the insufficient thickness of the material, then the highest IPCE is observed at the smallest wavelength (at $\lambda = 300$ nm in case of 0.55 and 0.67 μm thick nanotube layers), corresponding to the highest absorption coefficient. On the other hand, when the thickness of the nanotube layer becomes sufficient for complete absorption of the light, the IPCE is determined by the light penetration depth into the material: the deeper below the surface of the material the light is absorbed, the closer to the back-contact of the electrode the charge carriers are generated, resulting in smaller recombination losses. Thus, the IPCE maximum shifts to the largest wavelength at which a complete light absorption is possible.

While light absorption efficiency is expected to increase with the thickness of nanotube layers [30] due to a longer absorption length within the material, the longer is the diffusion path for electrons to reach the back contact of the electrode - this leads to higher transport resistance and recombination losses [33]. From Fig. 2b it is evident that the presence of MeOH significantly increases the magnitude of the photocurrent, while the spectral features remain unchanged. However, the length of the tubes does not significantly affect the maximum IPCE. This holds also for other hole capture agents, as shown in the SI (Fig. S3).

The higher IPCE in the presence of MeOH can be attributed to the effective scavenging of holes by its molecules, resulting in decreased recombination losses. Besides that, the positive effect of MeOH on the photocurrent has been also attributed to a current doubling effect (direct oxidation of methanol radical $\bullet\text{CH}_2\text{OH}$ at the electrode surface leading to an additional free electron) [33].

The results corresponding to Fig. 3a and 3b are summarized in Table 1. It is evident that: 1) the length of the TiO_2 nanotubes strongly influences the IPCE spectra in absence of MeOH; 2) the presence of a hole capture agent leads to higher IPCE, but the IPCE does not depend on the thickness of the nanotube layers for all irradiation wavelengths.

In order to estimate the band gap for the TiO_2 nanotube layers the data was plotted as $(I_{\text{ph}} h\nu)^{1/2}$ vs. $h\nu$ (h is the Planck constant, ν is the frequency of the light) using the data from the photocurrent spectra of the TiO_2 nanotubes in the hole scavenger free (Fig 2c) and in the MeOH-containing (Fig 2d) electrolytes. The obtained band gap values for nanotubes of different lengths and in different electrolytes are all in range of 3.02–3.13 eV, which roughly is consistent with the previously reported values for anodic TiO_2 nanotubes [2].

Table 1

IPCE spectra of the 4.58 μm thick TiO_2 nanotube layers (selected because of the highest IPCE in the Na_2SO_4 electrolyte) were taken to compare different hole scavengers (Fig. 4). It is worth mentioning that in the wavelength range of 300 - 600 nm, no noticeable change in light absorption for the different electrolytes could be detected by UV-vis spectrometry (i.e., the absorption of the different electrolytes does not interfere with the measurements). From Fig. 4 on can see that in comparison to the reference electrolyte, significantly higher IPCE values are observed in the presence of the tested hole scavengers, which can be ranked as follows: EDTA- Na_2 ($\text{IPCE}_{\text{max}} = 53\%$) > EG ($\text{IPCE}_{\text{max}} = 50\%$) > MeOH ($\text{IPCE}_{\text{max}} = 43\%$) > i-PrOH ($\text{IPCE}_{\text{max}} = 40\%$) > Na_2SO_3 ($\text{IPCE}_{\text{max}} = 32\%$) > no hole scavengers ($\text{IPCE}_{\text{max}} = 17\%$). This result confirms the ability of the selected additives to scavenge the photogenerated holes from the surface of TiO_2 nanotubes, thus preventing their recombination with electrons and allowing the latter to contribute to the photocurrent. Moreover, as mentioned above, in the presence of organic hole scavengers the current doubling effect may be possible via the formation of unstable radicals, followed by an electron injection into the conduction band of a photocatalyst [34].

Fig.4

Significant effects of hole scavengers are also evident from the photocurrent transients. Fig. 5 shows the transient behavior of the photocurrent using the 4.58 μm long TiO_2 nanotubes irradiated at a wavelength of 350 nm at different external voltages. For these measurements, first the voltage was decreased from 0.5 V in 0.05 V steps until the optical flatband (photocurrent onset) potential was reached; then, the voltage was switched to 0.55 V and further increased in 0.05 V steps until the value of 1 V. In Fig. 5, the slight glitch in the data at 0.55 V stems from the way the measurement was conducted, i.e. switching the external voltage directly from the flat-band voltage to 0.55 V.

As can be seen from the Fig. 5a, in the absence of hole scavengers pronounced positive spikes are observed in the current transients over the whole range of applied voltages. These initial spikes are higher at voltages below 0.3 V. According to literature [35], such positive spikes in the current transients (observed upon turning the light on) are a result of an accumulation of holes at the electrode/electrolyte interface.

Negative spikes (upon turning the light off) in the current transients are observed at voltages ≤ 0.2 V (emptying of states in the dark), whereas above 0.25 V both saturation of the photocurrent and disappearance of the negative spikes occur. This indicates that at voltages ≤ 0.2 V the charge depletion layer thickness in TiO₂ nanotubes is smaller than half the characteristic thickness of the components (tube walls), therefore the photogenerated holes rapidly recombine in the regions of the material that does not experience beneficial space charge effects, i.e. are non-depleted of the majority carriers (electrons). At voltages above 0.2 V the recombination is suppressed due to a complete depletion of electrons within the material [31].

As shown before and as expected, the addition of hole scavengers to the electrolytes results in a significant photocurrent increase (as additionally shown in Fig. 6), along with a drastic reduction in the intensity of the spikes on the current transients (Fig 5b-f), which indicates the suppression of both accumulation and recombination of charge carriers. The onset potential (vs. Ag/AgCl) for the photocurrent shifts from approx. -0.152 V (in the hole scavenger free electrolyte) to the cathodic direction in the presence of hole scavengers, reaching values of approx. -0.426 V (for MeOH), -0.347 V (for i-PrOH), -0.529 V (for EG), -0.477 V (for EDTA-Na₂) and -0.701 V (for Na₂SO₃). This shift indicates that the injection barrier (kinetic or thermodynamic) for the holes to the electrolyte has been lowered by the presence of all hole capture agents, resulting in a higher hole transfer rate to hole scavengers than to OH⁻ [35,36]. As a result of the changed injection barrier, the observed photocurrent

onset potential and thus changed optical flatband potential of the electrode material vary for the different hole capture agents. In fact, these findings are in excellent agreement with literature [37] that reports a flatband potential of an anatase single-crystal electrode at pH 7 at approx. -0.768 V (vs. Ag/AgCl) in 1 M H₂SO₄ electrolyte. Nevertheless, up to 0.26 V higher flatband potentials have also been reported in [38] for anatase thin films, and in [39] a flatband potential of -0.57 V (vs. Ag/AgCl) was reported for anatase TiO₂ nanotubes in a deaerated 1 M (NH₄)₂SO₄ electrolyte.

The difference between the photocurrent onset potentials in the presence of EG (-0.529 V), MeOH (-0.426 V), and i-PrOH (-0.347 V) (each electrolyte has pH 7) can be related to the difference in their red-ox potentials (E_{ox}): EG ($E_{ox} = 0.009$ V vs. NHE [40]) < MeOH ($E_{ox} = 0.016$ V vs. NHE [40]) < i-PrOH ($E_{ox} = 0.105$ V vs. NHE [40]). This would be in line with the common approach that the red-ox potential of the electrolyte determines the flatband potential of a semiconductor/electrolyte-junction [41]. This may be different for species such as EDTA that have a strong surface complexing ability with TiO₂. In this case, band-edge pinning may have been altered – this would explain why the shift in the photocurrent onset potential is different from plain alcohols [41].

Fig.5

Fig.6

Finally, we compared the influence of hole scavengers on the H₂ production rate under ocp conditions - that is, under plain photocatalytic conditions. In every case, the ocp's of the Pt-decorated tubes in the dark were positive to the flatband potential, as shown in Table 2.

Table 2

The amounts of H₂ produced by Pt-decorated TiO₂ nanotubes in the presence of the selected hole scavengers are compared in Fig. 7. Pt decoration on the tubes was used to

provide a defined electron transfer to the electrolyte. The largest volume of H₂ evolved in the presence of MeOH (372.1 μ L), which is followed by i-PrOH (315.2 μ L), EDTA-Na₂ (309.2 μ L) and EG (129.6 μ L). In the presence of Na₂SO₃, however, only 6 μ L of H₂ was produced, which is 2.15 times less than in the hole scavenger free 0.1 M Na₂SO₄ electrolyte (12.9 μ L). It should be mentioned that certain hole scavengers are known to produce H₂ in the absence of any photocatalysts, for example by light-induced decomposition [15,42]. In our example, the contribution of this reaction to the overall H₂ evolution is significant only under irradiation at wavelengths below 300 nm [42], and therefore such short wavelengths were not considered in this work.

Fig.7

For powders, a wide range of factors have been described, such as thermodynamics, polarization, interaction of the hole scavengers (and their oxidation products) with the surface of the photocatalyst, their composition (namely, hydrogen content and state, as well as C:O atomic ratios in organic hole scavengers), and acidity of the reaction medium (determining the availability of protons for reduction by the photogenerated electrons). For example, in [42] the amounts of H₂ photocatalytically produced by Pt/TiO₂ nanoparticles in the presence of different hole scavengers ranked as follows: 1183.8 μ mol (in 0.1 M MeOH) > 508.2 μ mol (in 0.1 M EDTA-Na) > 15.9 μ mol (in 0.1 M Na₂SO₃). In another study on H₂ production by Pt/TiO₂ powders [11] the latter performed significantly better in the presence of MeOH (11.5 mmol H₂), than in the presence of EDTA (2.209 mmol H₂), Na₂S (1.232 mmol H₂) or Na₂IO₃ (0.0051 mmol H₂). Similarly, in [12] the amounts of H₂ produced by Pt/TiO₂ nanoparticles in 2.5 M MeOH were higher than in 10 mM EDTA or 10 mM formic acid, although it has been ascribed to higher concentration of MeOH. On the contrary, in [43] for H₂ evolution by a mixture of RuO₂/TiO₂ and TiO₂ powders at pH = 1, a slightly different trend (positive effect of hole scavengers ranking as follows: EDTA > MeOH > ethanol > lactic acid) was observed.

In [44] the H₂ evolution performance of Pt/TiO₂ powders in the presence of alcohols has been found to correlate with their polarities (higher polarity leading to higher H₂ evolution rate: MeOH > ethanol > 1-propanol > 2-propanol > butanol). In [45] the H₂ evolution rates over Pd/TiO₂ nanoparticles have been found to follow the stoichiometry of the photoreforming reaction of the hole scavengers: H₂ volume (per mol of EG) > H₂ volume (per mol of i-PrOH) > H₂ volume (per mol of MeOH). The authors suggested the additional H₂ evolution pathway for i-PrOH via oxidation of methyl groups, as well as a possible poisoning of the Pd surface by strongly bound CO derived from MeOH decomposition.

Thermodynamically, one of the factors determining the positive effect of different hole scavengers on the photocatalytic H₂ evolution rate is how their oxidation potential compares to that of water. As was mentioned before, the oxidation potential of the molecule determines the driving force of hole scavenging: more negative oxidation potential (vs. NHE) leads to faster hole scavenging and vice versa [7,41]. Therefore, hole scavengers having more negative (vs. NHE) redox potential than water can capture photogenerated holes much faster, leading to increased H₂ evolution rates due to decreased recombination losses of electrons. Besides that, the competition for holes between hole scavengers and OH⁻/H₂O also leads to the suppression of the O₂ evolution reaction, thus preventing the back reaction of O₂ with H₂ at Pt (leading to production of water). Accordingly, almost linear increase in H₂ evolution rates by Pt/TiO₂ nanoparticles with decreasing exponential of the redox potential (vs. NHE) of an alcohol (utilized as a hole scavenger) was observed in [40], the linear dependence being best followed for alcohols having the same C:O atomic ratios. In our case, however, this trend is confirmed only for MeOH ($E_{ox} = 0.016$ V vs. NHE [40]) and i-PrOH ($E_{ox} = 0.105$ V vs. NHE [40]), while EG ($E_{ox} = 0.009$ V vs. NHE [40]), EDTA-Na₂ ($E_{ox} = -0.5$ V vs NHE [7]) and Na₂SO₃ ($E_{ox} = -1.5$ V vs NHE [7]) are the exceptions from this trend. Thus, in these cases it is

possible that besides the oxidation potential of a hole scavenger, other factors play a major role.

In the EDTA case, strong surface adsorption leads to species forming inner-sphere complexes on the surface of TiO₂ (such as oxalic and formic acid) that can be directly oxidized by valence band holes, while in case of weaker interaction with TiO₂ via hydrogen bonds, hole scavengers are less effective due to outer sphere reactions, the latter reaction being less effective and resulting in slower H₂ evolution rates [46]. On the other hand, excessive adsorption of hole scavengers may lead to the occupation of active sites at the surface of a photocatalyst leaving no available sites for H₂ evolution [15], and the decreased H₂ evolution rates by Ce-doped TiO₂ nanoparticles at high sulfite ion concentrations were also observed in [24]. This may explain the detrimental effect of Na₂SO₃ on the H₂ evolution observed in the present study.

Besides the hole capturing role, which allows more H₂ to be produced via the reduction of protons from water by photogenerated electrons, many organic compounds can also yield H₂ as one of the products of their photocatalytic degradation (photoreforming) reaction [18]. This may alternatively explain low H₂ evolution performance in the presence of Na₂SO₃, which cannot serve as a source of H₂.

Overall, it is noteworthy that the efficiency of the different hole capture agents for the photocurrent generation (photoelectrochemical conditions) and for the photocatalytic H₂ production (open circuit conditions) is substantially different. In the latter case, while certain trends previously reported for Pt/TiO₂ nanoparticles have been also observed for Pt-decorated TiO₂ nanotubes (such as the higher H₂ evolution performance in the presence of MeOH, than in the presence of i-PrOH, EDTA-Na₂ and Na₂SO₃), deviations from these trends (such as unexpectedly low amount of H₂ produced in the presence of EG) point out that for TiO₂

nanotubes the efficiencies of hole scavengers are determined by factors specific to the nature of the nanotubes.

4. Conclusions

While ample of research is available on the effects of sacrificial agents on the activity of TiO_2 nanoparticles, this is not the case for anodic TiO_2 nanotubes, either used as a photoanode or used under photocatalytic conditions. Therefore we studied the effect of selected organic (MeOH , $i\text{-PrOH}$, EG , EDTA-Na_2) and inorganic (Na_2SO_3) hole scavengers on various length of anodic nanotubes. We find that the photoelectrochemical response (IPCE) increases in the sequence $\text{Na}_2\text{SO}_3 < \text{isopropanol} < \text{MeOH} < \text{ethylene glycol} < \text{EDTA-Na}_2$. The ability of the selected additives to scavenge photogenerated holes is also evident from significant changes in the photocurrent transients in comparison to the reference Na_2SO_4 solution. The presence of sacrificial agents also leads to a cathodic shift of the onset potential of the photocurrent, which to a large extent can be explained by the different red-ox potentials of the additives.

Measurements of the photocatalytic H_2 evolution using Pt-decorated anodic TiO_2 nanotubes showed a H_2 production performance that increased up to 28.8 times in the presence of MeOH . The sequence of effectiveness is $\text{MeOH} > i\text{-PrOH} > \text{EDTA-Na}_2 > \text{EG}$, while a detrimental effect of Na_2SO_3 is observed.

The changes in the sequence (photoelectrochemical vs. photocatalytic) and the detrimental effect of Na_2SO_3 on the H_2 evolution performance point out the importance of selecting appropriate hole scavengers and reaction conditions (hole scavenger concentration, pH) based on the properties and intended applications of a photocatalyst, and illustrate the challenges involved in comparing data measured for different sacrificial agents and different experimental targets.

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Fig. 1

Fig. 1. (a–c) SEM images of the surface (a) and the cross-section (b) of the pristine (a, b) and Pt-decorated (c) TiO₂ nanotubes (10 min anodization); (d) XRD patterns of the as-formed (after anodization), annealed at 450°C and Pt-decorated (after annealing) TiO₂ nanotube layers; (e, f) TEM cross-sectional images of Pt-decorated TiO₂ nanotubes: e – the top part (Pt-decorated tips of the nanotubes), f – the middle part (nanotube wall).

Fig. 2

Fig. 2. (a, b) IPCE spectra of the TiO₂ nanotubes in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ + 20 vol.% MeOH; (c, d) $(I_{ph} h\nu)^{1/2}$ vs. $h\nu$ plots derived from the photocurrent spectra of TiO₂ nanotubes in (c) 0.1 M Na₂SO₄ and (d) 0.1 M Na₂SO₄ + 20 vol.% MeOH.

Fig. 3

Fig. 3. Schematic representation of the wavelength dependence of the absorption coefficient of TiO₂ versus the carrier diffusion length for anodic TiO₂ nanotubes. (a) The absorption coefficient is relatively small for the light of longer wavelength, which results in larger absorption length of light within the material (L_a) and smaller diffusion length that the photogenerated electrons have to travel to reach the back-contact of the electrode (L_d); (b) For the shorter wavelength light the absorption coefficient is relatively large, which results in smaller L_a and larger L_d .

Fig. 4

Fig. 4. IPCE spectra of the 4.58 μm thick TiO_2 nanotube layers recorded at 0.5 V (vs. Ag/AgCl) in the 0.1 M Na_2SO_4 electrolytes containing one of the selected hole scavengers.

Fig. 5

Fig. 5. Chopped light photocurrent voltage curves of the 4.58 μm thick TiO_2 nanotubes in 0.1 M Na_2SO_4 solutions containing one of the selected hole scavengers: a) without hole scavengers; b) MeOH (10 vol.%); c) i-PrOH (10 vol.%); d) EG (10 vol.%); e) EDTA- Na_2 (0.1

M); f) Na_2SO_3 (0.1 M). Measurements were performed at voltages below 1 V (the values in V vs. Ag/AgCl are selectively indicated above the transients; the voltage difference between each transient is 0.05 V). The insets show magnified current transients at 0.2 V.

Fig. 6

Fig. 6. Steady-state photocurrent (irradiation wavelength $\lambda = 350$ nm) as a function of applied potential (vs. Ag/AgCl) of the TiO_2 nanotubes (10 min anodization) in 0.1 M Na_2SO_4 solutions containing one of the selected hole scavengers

Fig. 7

Fig. 7. Photocatalytic H_2 generation of Pt-decorated TiO_2 nanotubes irradiated for 3 h at $\lambda = 365$ nm in 0.1 M Na_2SO_4 solutions containing one of the selected hole scavengers.

Table 1. The effect of anodization duration on the thickness and maximum IPCE of the prepared TiO₂ nanotubes

Anodization duration, min	Thickness, μm	Maximum IPCE (wavelength) in 0.1 M Na₂SO₄	Maximum IPCE (wavelength) in 0.1 M Na₂SO₄ + 20 vol.% MeOH
0.5	0.55±0.21	17.40% (300 nm)	-
1	0.67±0.13	16.32% (300 nm)	-
2.5	1.04±0.04	15.67% (330 nm)	-
5	2.19±0.31	16.86% (350 nm)	39.23% (350 nm)
10	4.58±0.65	17.27% (355 nm)	43.34% (350 nm)
20	7.89±0.6	16.21% (360 nm)	41.21% (355 nm)
30	10.88±0.53	14.38% (360 nm)	39.07% (355 nm)

Table 2. Open circuit potentials of the TiO₂ nanotubes in dark in the air-saturated solutions containing different hole scavengers

Solution composition	ocp, V vs. Ag/AgCl
0.1 M Na ₂ SO ₄	-0.14
0.1 M Na ₂ SO ₄ + 10 vol.% MeOH	0.038
0.1 M Na ₂ SO ₄ + 10 vol.% i-PrOH	0.091
0.1 M Na ₂ SO ₄ + 10 vol.% EG	0.046
0.1 M Na ₂ SO ₄ + 0.1 M EDTA-Na ₂	0.002
0.1 M Na ₂ SO ₄ + 0.1 M Na ₂ SO ₃	0.063

Supplementary information

Effect of different hole scavengers on the photoelectrochemical properties and photocatalytic hydrogen evolution performance of pristine and Pt-decorated TiO₂ nanotubes

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Figure S1. SEM images of the surface (on the left) and the cross-sections (on the right) of the porous layers formed by anodization of Ti foils for: a, b – 0.5 min; c, d – 1 min; e, f – 2.5 min; g, h – 5 min; i, j – 20 min; k, l – 30 min

Fig S2. (a) XPS spectrum of the Pt-decorated TiO₂ nanotubes; (b) High-resolution XPS of Pt4f spectrum of Pt-decorated TiO₂ nanotubes.

Fig. S3. IPCE spectra of the TiO₂ nanotubes in (a) 0.1 M Na₂SO₄ + 20 vol.% i-PrOH and (b) 0.1 M Na₂SO₄ + 20 vol.% EG.