Photoelectrochemical properties of “increasingly dark” TiO₂ nanotube arrays

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Abstract

“Black” TiO₂ nanotube arrays (TNTAs) of different darkness are formed by thermal reduction of anodic TiO₂ nanotube layers in H₂ atmosphere at different temperatures (300–500°C), and their (photo-)electrochemical properties are studied by IPCE spectroscopy, transient photocurrent measurements, IMPS, PEIS, and Mott-Schottky analysis. Hydrogenation of the TNTAs leads to the enhancement of their IPCE (by up to 1.5 times), despite increased recombination losses at anodic potentials. Reduced TNTAs demonstrate a “metallic” behavior by a characteristic frequency response of their impedance and phase angle, reduced charge transfer resistance at anodic bias, increased double layer capacitance, and remarkably increased donor densities (up to $7.25 \times 10^{23} \text{ cm}^{-3}$). The observed alterations in the properties of TNTAs after hydrogenation are ascribed to the formation of defects and TiH_x.

Keywords: anodization, TiO₂, nanotubes, hydrogenation, black titania, photoelectrochemistry

1. Introduction

Titanium dioxide (TiO₂) is often considered a very promising light harvesting material owing to its adequate photochemical and photocurrent response to UV light, photo- and chemical stability, low cost, and non-toxicity. Moreover, its band-edge positions are suitable for certain useful electron transfer reactions, such as decomposition of H₂O to H₂ and O₂ or creation of •OH radicals [1]. As a consequence, photoelectrochemical properties of TiO₂ in its various forms, as well as in combination with other materials, have been widely investigated, and massive efforts are made to improve the performance of TiO₂-based photoelectrochemical devices. Some of them are aimed at fostering the adsorption of species from the electrolyte and the consequent charge transfer processes on the electrode/electrolyte interface via maximizing the surface area of the TiO₂ electrodes, which can be achieved by creating nanostructured forms of TiO₂. Among the latter, arguably the most fascinating are self-organized TiO₂ nanotube arrays (TNTAs), which represent a unique combination of the highly functional features of TiO₂ with a regular and

controllable nanoscale geometry [2]. Highly ordered arrays of TiO₂ nanotubes can be formed on Ti substrates by anodizing them in water- or organic-based electrolytes. Depending on the anodizing parameters, different morphologies can be obtained, e.g. spaced or close-packed tubes, single- or double-walled tubes, smooth-walled or bamboo-type tubes, as well as branched or stacked tubes [3–6]. Good electrical contact to the Ti substrate and outstanding electron diffusion length (reaching 100 μm [7]) along the tube walls make TNTAs a promising material for application in photoelectrochemical devices.

Besides a large surface area accessible for adsorption and charge transfer, a high degree of crystallinity is often seen as a crucial factor in achieving effective utilization of absorbed light by TiO₂. It is well known that imperfections in the crystalline lattice (e.g. point defects) can act as recombination sites for the photogenerated charge carriers, causing a significant loss of performance. On the other hand, defect engineering has recently been recognized as a viable approach to optimization of key performance-related properties of TiO₂, including the band gap, Fermi level, concentration of surface active sites and charge transport [8]. Introduction of intrinsic defects, such as Ti³⁺ or oxygen vacancies, into the crystalline lattice of TiO₂ leads to a modification of its band gap (e.g. formation of allowed states). As a consequence, the optical absorption edge of TiO₂ materials can be shifted to visible or even infrared [9] region, making them especially interesting for solar energy conversion applications.

Defective TiO₂ nanomaterials can be synthesized by numerous methods, which have been well-reviewed in [10–13]. For instance, intrinsic defects can be introduced into crystallized TiO₂ by applying reductive treatments (e.g. oxygen-deficient atmosphere combined with high temperature or plasma treatment, as well as chemical and electrochemical reduction). Similarly, “black” TiO₂ (TiO_x) nanotube arrays have been previously synthesized by high [14] or ambient [15–18] pressure heat treatment in H₂ [14,18] or Ar/H₂ [15,17] atmosphere, high-energy proton implantation [19], soaking in an NH₄F-containing ethylene glycol [20] and electrochemical reduction (“self-doping”) [21,22]. Promisingly, enhanced photocurrent [15,18,20,21] and

photocatalytic activity (e.g. in H₂ evolution [14,19] and degradation of organic compounds [16,17,20,21]) under solar simulated irradiation has been reported for the reduced TNTAs.

While several studies have carried out photoelectrochemical studies of reduced (hydrogenated) TiO₂ nanomaterials, very limited knowledge on detailed photoelectrochemical behaviour of differently reduced TiO₂ nanotubes has been accumulated so far. Therefore, in this work we perform thermal reduction of anodic TNTAs in pure H₂ atmosphere at different temperatures (leading to different defect structures [23]) and systematically study their subsequent photoelectrochemical properties by IPCE spectroscopy, transient photocurrent measurements, IMPS, PEIS, and Mott-Schottky analysis.

2. Experimental

The TNTAs (4.5 μm tube length) were grown by anodizing (anodization area of 0.785 cm²) the Ti foils (0.1 mm thick, 99.6% pure temper annealed, ADVENT) in an electrolyte containing ethylene glycol, 0.15 M NH₄F and 3 vol% of deionized water at a constant potential of 60 V for 10 min at room temperature. After anodization the TNTAs were rinsed with ethanol and annealed at 450°C for 1 h in air. Finally, the reduction of TNTAs was performed by thermal treatment in a tubular furnace under constant H₂ flow at 300°C, 400°C, 450°C, or 500°C for 10-60 min. Thus, the prepared samples will be further identified as “untreated”, “300-1h”, “400-1h”, “450-10min”, “450-30min”, and “500-1h”, respectively.

The morphology of the prepared samples was studied by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800).

The crystal structure of the TNTAs was studied by X-ray diffraction (XRD, X'pert Philips MPD with a Panalytical X'celerator detector) using graphite monochromatized Cu Kα radiation (wavelength 1.5406 Å). The approximate crystallite size was determined from the peak broadening of XRD reflections by the Scherrer formula [24] 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), β is the full width at half-maximum (FWHM) in X-ray diffraction reflections of the anatase (101) peak of TiO₂, and θ is the Bragg angle.

Electrochemical (incl. photoelectrochemical) measurements (IPCE, transient photocurrent response, IMPS, PEIS, Mott-Schottky analysis) were performed in a 3-electrode cell, which consisted of a TNTAs sample as a working electrode, Pt wire as a counter electrode, and Ag/AgCl reference electrode. As an electrolyte a 0.1 M Na₂SO₄ aqueous solution was used. The area of each sample subjected to irradiation and to the electrolyte was 0.5 cm².

Incident photon-to-current conversion efficiency (IPCE) spectra were recorded at a constant potential of 0.5 V (vs. Ag/AgCl) in the illumination wavelength range of 300–600 nm using an Oriel 6365 150 W Xe-lamp equipped with an Oriel Cornerstone 7400 1/8 m monochromator as a light source. The IPCE of the TNTAs was calculated at each wavelength using Eq. (2) below:

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

where j_{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).

Transient photocurrent response was measured at constant potentials in the range of -0.5–1 V (vs. Ag/AgCl) at $\lambda = 350$ nm (light power density of 2.5 W/m²) using the same light source, as during the IPCE measurements. During the measurements the samples were irradiated in the following sequence: light off (10 s); light on (20 s); light off (10 s).

Intensity-modulated photocurrent spectroscopy (IMPS) measurements were carried out under constant potentials in the range of 0–0.5 V (vs. Ag/AgCl) using a Zahner IM6 (Zahner Elektrik, Kronach, Germany) with a tunable TLS03 UV and visible-light source. Light with $\lambda = 358$ nm and the power density of 10 W/m² was used as a base, on which a sinusoidal modulation of the light power density with the amplitude of 1 W/m² was superimposed, so that the overall

power density of the illumination oscillated in the range of 9–11 W/m². The frequency range of oscillations was 10⁻²-10³ Hz.

Photoelectrochemical impedance spectroscopy (PEIS) studies were performed under potentials in the range of 0–0.5 V (vs. Ag/AgCl) and under illumination with a constant power density of 36 W/m² at $\lambda = 369$ nm. Sinusoidal modulation of the applied potential with an amplitude of 10 mV was performed in the frequency range of 10⁻¹-10⁵ Hz.

Mott-Schottky analysis was performed in the dark by sweeping the applied potential from 0.5 V to -0.5 V (vs. Ag/AgCl). Sinusoidal modulation of the applied potential with an amplitude of 10 mV was performed at selected frequencies in the range of 10⁻²-10⁴ Hz. The donor density (N_d) was calculated by the equation (3):

$$N_d = (2/e_0\epsilon\epsilon_0)[d(C^{-2})/dV]^{-1} \quad (3)$$

where e_0 is the electron charge (1.6×10^{-19} C), ϵ is the dielectric constant of TiO₂ ($\epsilon = 55$ for anatase thin films [25]), ϵ_0 is the permittivity of vacuum (8.85×10^{-12} Fm⁻¹), and C is the capacitance derived from the electrochemical impedance at each potential (V). The $d(C^{-2})/dV$ values were determined from the slope of the linear parts of the Mott-Schottky plots.

3. Results and discussion

First screening of the samples after different thermal treatments showed some expected changes in the appearance of the samples. After hydrogenation at moderate temperatures, the samples remained visually unchanged (for 300-1h, 400-1h and 450-10min samples). Apparent color change of the anodized areas was observed only for 450-30min (to light-blue color) and 500-1h (to black color) samples.

SEM images of the TNTAs are shown in Fig. 1a–c and Fig. S1. For all samples, a 3.8–4.5 μ m thick layer of close-packed TNTAs (Fig. 1c) has been formed below a typical initiation layer, with no noticeable differences in the surface morphology before and after thermal treatment.

Fig. 1. (a-c) SEM images of the surface (a, b) and cross-section (c) of the TNTAs samples: (a, c) untreated, (b) 500-1h; (d) XRD patterns of the hydrogenated TNTAs samples

XRD measurements were performed in order to identify the phase composition of the hydrogenated TNTAs, and the corresponding spectra are shown in Fig. 1d. Besides the Ti signal from the substrate, all samples predominantly consist of anatase TiO_2 with an average crystallite size of 20.9 nm as calculated from the Scherrer equation. Additional peaks at 35° (as evidenced by the enhanced intensity of the Ti (100) peak at the same Bragg angle), 41° , and 60° observed for the 450-30min and 500-1h samples are commonly ascribed to TiH_x . Interestingly, no TiH_x peaks were observed in the previous studies for TiO_2 hydrogenated in pure H_2 at 20 bar (at 500°C for 1 h) [14], in pure H_2 at ambient pressure (at $300\text{--}550^\circ\text{C}$ for 30 min) [18], or in $\text{H}_2(10\%)\text{-Ar}$ at ambient pressure (at 800°C for 2 h) [26]. The Cu signal for the 500-1h sample stems from a sputter-

coated Cu layer deposited on the backside and around the anodized area of the sample, in order to protect the unanodized Ti sample from H₂ embrittlement.

After thermal treatments, incident-photon-to-current efficiency (IPCE) measurements were carried out. The IPCE spectra of the TNTAs are shown in Fig. 2, and the peak IPCE values are summarized in Table 1. The highest IPCE of 53% was demonstrated by the TNTAs hydrogenated at 300°C for 1 h, and, overall, hydrogenation at lower temperatures (300–450°C) leads to 1.2-1.5 times IPCE increase in comparison to the untreated TNTAs. Similarly, enhanced photocurrent generation by the reduced (hydrogenated) TiO₂ has been reported in [18,27–29]. Increasing hydrogenation time at 450°C (from 10 min to 30 min), as well as further increasing the hydrogenation temperature to 500°C leads to IPCE deterioration. Similar IPCE decrease above certain hydrogenation temperature (e.g. 300°C [28], 350°C [18], or 400°C [29]) has been previously observed for TiO₂. It was suggested in Ref. [10] that surface oxygen vacancies and Ti³⁺ states are responsible for the increased photocatalytic activity (via facilitating charge carrier separation), while in the bulk these defects act as trap states and charge carrier recombination centers. Thus, in our case it is possible that hydrogenation at moderate temperatures (below 500°C) induces the formation of defects mainly on the surface of the TNTAs, which leads to the enhanced IPCE. Very low IPCE (< 1 %) in the visible range of the spectra was observed for all samples, similarly to [18,28]. Poor photocurrent generation performance of black TiO₂ in the visible light range (despite significant visible light absorption) has been found to be related to the short lifetime of charge carriers generated by visible light photons due to fast recombination on the trap states below oxygen vacancy level in the band gap of TiO₂, while significantly slower relaxation to the oxygen vacancy level was confirmed for the charge carriers generated by UV photons [30].

Fig. 2. IPCE spectra of the hydrogenated TNTAs recorded at 0.5 V (vs. Ag/AgCl) in 0.1 M Na₂SO₄. The inset shows the magnified part of the spectra (visible light region).

Table 1. Peak IPCE values and flat band potentials of the hydrogenated TNTAs

Sample	IPCE (%)	E_{fb} (V vs. Ag/AgCl)
untreated	34.8	-0.4
300-1h	52.6	-0.41
400-1h	43	-0.41
450-10min	47.2	-0.36
450-30min	41.4	-0.35
500-1h	23.9	-0.27

Transient photocurrent density measurements under monochromatic irradiation at $\lambda = 350$ nm were performed in order to analyze the kinetics of the current response of the TNTAs under chopped-light illumination at different potentials, and the results are shown in Fig. 3. The positive current spikes observed upon turning the light on are due to the flow and accumulation of holes at the electrode/electrolyte interface, while the negative spikes upon turning the light off represent the flow of electrons to the surface leading to recombination of the photogenerated charge carriers [31]. From the ratio of the steady-state photocurrent density under illumination (j_{ss}) and the

immediate photocurrent density after switching on the light ($j_{t=0}$), the transfer efficiency (η_{trans}) across the electrode/electrolyte interface can be calculated as follows [32]:

$$\eta_{\text{trans}} = j_{\text{ss}} / j_{t=0} = k_{\text{trans}} / (k_{\text{trans}} + k_{\text{rec}}) \quad (4)$$

The above equation also allows to calculate the $k_{\text{trans}} / k_{\text{rec}}$ ratios (for the cases of $j_{t=0} > j_{\text{ss}}$), where k_{trans} is the rate constant of hole transfer, and k_{rec} is the rate constant of hole recombination. Thus determined η_{trans} and $k_{\text{trans}} / k_{\text{rec}}$ values at different potentials for the hydrogenated TNTAs were plotted in Fig. 4. For the untreated and the 300-1h samples η_{trans} reaches 100% at 0.4 and 0.45 V, respectively, which indicates that the surface of TNTAs becomes sufficiently depleted of electrons at these potentials and the recombination is almost completely suppressed. On the other hand, for the 400-1h and 500-1h samples η_{trans} does not exceed 95% even at 1 V. Evidently, introduction of defects into TiO_2 lattice affects the competition between the recombination and the charge transfer to the electrolyte. Apparently, increased recombination rates in the hydrogenated TNTAs lead to the anodic shift of the corresponding j_{ss} saturation potentials, and thus, it can be expected that higher j_{ss} values would be generated by these samples at potentials above 1 V.

Fig. 3. Transient photocurrent response of the hydrogenated TNTAs at $\lambda = 350 nm$ and at a constant potential in the range of -0.5–1 V vs. Ag/AgCl (the applied potential is selectively indicated above the transients, and the step between each transient is 0.05 V) in 0.1 M Na_2SO_4 .

Fig. 4. η_{trans} (a) and $k_{\text{trans}} / k_{\text{rec}}$ (b) vs. potential curves calculated from the transient photocurrent response of the hydrogenated TNTAs

Based on the transient photocurrent density measurements, j_{ss} vs. potential curves are shown in Fig. 5. While relatively small dispersion in j_{ss} values between the samples is observed at -0.2–0 V, significant differences in j_{ss} behavior can be seen at anodic bias, which correlate with η_{trans} ($k_{\text{trans}} / k_{\text{rec}}$) vs. potential curves. With higher potential fast j_{ss} increase until saturation is observed for untreated and 300-1h samples, while the samples hydrogenated at higher temperatures show much slower increase without reaching the saturation. In agreement with the IPCE measurements, the 300-1h sample shows the highest j_{ss} at -0.2–0.8 V. Interestingly, at 0.8–1 V the 400-1h, 450-10min and 450-30min samples begin to outperform the 300-1h sample (which has already reached its maximum j_{ss} at 0.5 V), indicating that the initial photon-to-current conversion efficiency (before recombination) is higher for the samples hydrogenated at 400–450°C. From the j_{ss} vs. potential curves the flat band potential (E_{fb}) of the TNTAs can be determined as being equal to the onset potential of the steady-state photocurrent. In contrast to our previous work [33], in the present work the potential was changed stepwise from -0.5 to 1 V in order to avoid the formation of stable peroxide surface states under illumination at anodic bias [34], which could cause a significant reduction current at cathodic bias [35]. The determined E_{fb} values are summarized in Table 1. Overall, relatively similar values of E_{fb} are observed for all

samples with only a slight shift to the anodic direction (from -0.4 V to -0.27 V vs. Ag/AgCl) with increasing the hydrogenation temperature.

Fig. 5. Steady-state photocurrent density vs. potential curves of the hydrogenated TNTAs at $\lambda = 350$ nm in 0.1 M Na_2SO_4 .

IMPS measurements were carried out in order to evaluate the kinetics of electron-hole recombination in the TNTAs, as well as of charge transfer across the semiconductor/electrolyte interface. In contrast to transient photocurrent measurements, during which the illumination conditions are changed drastically (from 0 to 2.5 W/m^2 at $\lambda = 350$ nm), IMPS measurements are based on a relatively small amplitude ($\sim 10\%$) sinusoidal oscillations of the light intensity under constant illumination (10 W/m^2 at $\lambda = 358$ nm). This allows to avoid certain effects caused by drastic changes in the amount of charge accumulated at the semiconductor/electrolyte interface, such as changes in the band bending [36]. The recorded IMPS plots are shown in Fig. 6. The upper semicircle of the plots corresponds to competition between charge transfer and recombination, while the lower semicircle corresponds to RC attenuation of the electrochemical cell [37]. The latter could result from the series resistance of the substrate (note that a comparably resistive rutile layer can form under the TNTAs during the annealing in air at temperatures close to 500°C due to

thermal oxidation of the Ti substrate [38]) and the space charge capacitance of the TNTAs. More details on the IMPS theory can be found in the works of Peter et al. [36,37].

Fig. 6. IMPS curves of the hydrogenated TNTAs recorded at 0–0.5 V vs. Ag/AgCl (as indicated above each curve) under illumination at $\lambda = 358$ nm in 0.1 M Na₂SO₄.

Using the parameters extracted from the upper semicircle of the IMPS curves, η_{trans} and k_{trans} / k_{rec} can be calculated as follows:

$$\eta_{\text{trans}} = j_{\text{LF}} / j_{\text{HF}} = k_{\text{trans}} / (k_{\text{trans}} + k_{\text{rec}}) \quad (5)$$

where j_{LF} is the lowest real photocurrent density recorded in the low frequency range, j_{HF} is the highest real photocurrent density (i.e. high frequency). The dependence of η_{trans} and $k_{\text{trans}} / k_{\text{rec}}$ on the applied potential is depicted in Fig. 7a–b. Compared to the η_{trans} curves calculated from the transient photocurrent (Fig. 4), a similar trend is observed. η_{trans} reaches its highest value of 98% for the untreated sample at 0.4 V, followed by the 300-1h (97% at 0.5 V), 500-1h (91% at 0.5 V) and 400-1h (85% at 0.5 V) samples. $k_{\text{trans}} / k_{\text{rec}}$ vs. potential curves (Fig. 7b) derived from the IMPS

data are very similar to the ones derived from the transient photocurrent response. Thus, a good correlation between the kinetic coefficients calculated from the transient photocurrent measurements and IMPS is observed. k_{trans} and k_{rec} can be further calculated using Eq. 5 and the following equation:

$$\omega_{\text{max}} = k_{\text{trans}} + k_{\text{rec}} \quad (6)$$

where ω_{max} is the radial frequency, at which the highest imaginary photocurrent density was recorded. The plots of k_{trans} and k_{rec} , vs. potential are shown in Fig. 7c–d. An overall decrease of k_{trans} with potential is observed for all samples (Fig. 7c), which indicates the decrease in surface concentration of electrons [36]. Similarly, k_{rec} decrease with potential (Fig. 7d) can be ascribed to recombination suppression due to the depletion of electrons in the TNTAs. As evident from the plots, k_{trans} and k_{rec} become less dependent on the applied potential with increasing the hydrogenation temperature of TNTAs. It was suggested in [39] that the thickness of the depleted region in TiO_2 becomes smaller with increasing the hydrogenation temperature, due to significant increase in donor density (which will be further discussed based on Mott-Schottky analysis). In our case, when the thickness of the depleted region becomes smaller than the tube wall thickness, high recombination rates would persist in non-depleted regions of the TNTAs. Thus, apparently, progressive thinning of the depleted region in the tube walls with the hydrogenation temperature leads to incomplete depletion of electrons in the TNTAs even at highly anodic potentials (as was also confirmed by the persistent transient photocurrent spikes), which explains the observed k_{trans} and k_{rec} vs. potential dependences.

Fig. 7. η_{trans} (a), $k_{\text{trans}} / k_{\text{rec}}$ (b), k_{trans} (c), and k_{rec} (d) vs. potential plots calculated from the IMPS curves of the hydrogenated TNTAs

The PEIS curves for the hydrogenated TNTAs recorded under illumination at different potentials are shown in Fig. 8a (at 0.5 V) and Fig. S2 (at 0–0.5 V). Based on PEIS curves recorded at 0.5 V, the results are shown in Bode plots (Fig. 8b–c) in order to show the frequency dependence of the absolute values of the impedance ($|Z|$) and of the phase angle (θ). Only one RC time constant is discernible for all samples, therefore, similarly to [26,27,40], the PEIS data was fitted by a simple equivalent circuit model (inset in Fig. 8b) consisting of series resistance (R_s), charge transfer resistance (R_{ct}) and a constant phase element (CPE). CPE was used to account for the non-ideal behavior of the double layer capacitance (C_{dl}) of the TNTAs, which was further calculated as follows:

$$C_{dl} = (Q_0 \times R_{ct})^{(1/n)} / R_{ct} \quad (7)$$

where Q_0 is the admittance of an ideal capacitor, and n is an empirical constant ($n = 0-1$). The electrical parameters of the TNTAs/electrolyte junction calculated from the PEIS curves (recorded at 0.5 V) are summarized in Table 2. Additionally, R_{ct} and C_{dl} vs. potential curves are shown in Fig. S3. Interestingly, the 300-1h sample shows the lowest R_{ct} at 0-0.3 V. It can be inferred that 300°C is an optimal hydrogenation temperature for achieving the improved charge transfer properties, which can be ascribed to charge carrier separation on the Ti^{3+} and oxygen vacancies [26]. R_{ct} values of the untreated and 300-1h samples increase with the applied potential, reaching 66.71 k Ω cm² and 10.53 k Ω cm² at 0.5 V, respectively, while relatively stable R_{ct} values below 6 k Ω cm² are observed for the samples hydrogenated at 400–500°C. This result further points out the reduced susceptibility of the hydrogenated TNTAs to charge carrier depletion by anodic polarization (or reduced thickness of the depleted region). Similarly, lower R_{ct} have been previously observed for hydrogenated TiO_2 [27]. Overall, low $|Z|$ and high θ values in the wider range of frequencies, as well higher C_{dl} values observed for the hydrogenated TNTAs point out a more capacitive behavior of the hydrogenated TNTAs/electrolyte junction in comparison to the untreated TNTAs/electrolyte junction. This can be ascribed to the increased conductivity of the reduced TiO_2 , which has been previously reported in [10,15].

Fig. 8. PEIS (a) and Bode (b,c) plots of the hydrogenated TNTAs at 0.5 V vs. Ag/AgCl (hollow symbols) fitted with an equivalent circuit model (solid lines). The insets (a,b) show the bottom-left part of the PEIS plots at higher magnification (a) and the equivalent circuit used as a model for fitting of the PEIS data (b).

Table 2. Electrical parameters of the hydrogenated TNTAs samples calculated by fitting the PEIS curves (recorded at 0.5 V vs. Ag/AgCl) with an equivalent circuit model

Sample	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($k\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)
untreated	26.39	66.71	2.43
300-1h	29.05	10.53	5.78
400-1h	26.97	4.38	393.04
450-10min	27.55	4.14	185.69
450-30min	31.7	3.3	488.97
500-1h	24.79	5.83	772.03

Mott-Schottky measurements were performed in order to estimate the donor density in the TNTAs, and the results are shown in Fig. 9 (at 500 Hz) and Fig. S4–S5 (at 0.01–10 kHz). Increasing the hydrogenation temperature leads to an increasingly noisy Mott-Schottky signal in the high-frequency range, which points out a “metallic” behavior of the reduced TNTAs. While

for the untreated sample a clear signal is observed even at 10 kHz, the 500-1h sample shows a smooth Mott-Schottky curve only at 10 Hz. Based on the curves recorded at 500 Hz, the N_d values were calculated using Eq. 3, and the results are summarized in Table 3. For the untreated sample $N_d = 3.89 \times 10^{18} \text{ cm}^{-3}$ was obtained, which is within the range of donor density values commonly reported for TiO_2 (approx. $10^{17} - 10^{19} \text{ cm}^{-3}$ [41]). A remarkable increase in the N_d can be seen for the reduced TNTAs, reaching $7.25 \times 10^{23} \text{ cm}^{-3}$ for the 500-1h sample. It can be ascribed to high concentrations of oxygen vacancies introduced by hydrogenation, which act as electron donors. Similarly, increased donor density values (e.g. up to $2.1 \times 10^{22} \text{ cm}^{-3}$ for hydrogenated TiO_2 [18], and $1.5 \times 10^{23} \text{ cm}^{-3}$ for TNTAs thermally reduced in vacuum at 450°C [42]) have been reported for reduced (hydrogenated) TiO_2 [26–29,39,43–45]. Significantly higher N_d values additionally explain the observed phenomena related to the increased recombination losses and lowered resistance, as, evidently, more electrons are able to recombine with holes and contribute to conductivity in the hydrogenated TNTAs.

Fig. 9. Mott-Schottky plots of the hydrogenated TNTAs recorded at 500 Hz in 0.1 M Na_2SO_4 . The inset shows the bottom part of the plots at higher magnification.

Table 3. Donor density values in the hydrogenated TNTAs samples calculated from the slopes of the Mott-Schottky plots (recorded at 500 Hz)

Sample	N_d (cm ⁻³)
untreated	3.89×10^{18}
300-1h	3.91×10^{19}
400-1h	1.38×10^{23}
450-10min	1.55×10^{22}
450-30min	2.05×10^{23}
500-1h	7.25×10^{23}

4. Conclusions

Detailed characterization of photoelectrochemical properties of thermally reduced anodic TiO₂ nanotube arrays was carried out. Hydrogenation at 300–500°C leads to significant changes in the photoelectrochemical properties of TNTAs, which can be ascribed to introduction of intrinsic defects into the TiO₂ lattice along with the formation of TiH_x phase. With increasing the hydrogenation temperature, the reduced TNTAs demonstrate increasingly more “metallic” properties, as reflected by significantly (by 1–5 orders) increased donor densities, lowered charge transfer resistance at anodic bias and high-frequency behavior of the impedance and phase angle. The introduced defect states can evidently act as recombination centers, lowering the charge transfer efficiency to the electrolyte even at highly anodic bias. Nevertheless, the increased recombination losses in the reduced TNTAs are compensated by up to 1.5 times improved IPCE in case of moderate hydrogenation temperatures (below 500°C).

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Photoelectrochemical properties of “increasingly dark” TiO₂ nanotube arrays

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Fig. S1. SEM images of the surface of the hydrogenated TNTAs samples: (a) 300-1h, (b) 400-1h; (c) 450-30min.

Fig S2. PEIS curves of the hydrogenated TNTAs recorded at different potentials (vs. Ag/AgCl). i- OCP – open circuit potential under illumination.

Fig S3. R_{ct} and C_{dl} vs. potential curves of the hydrogenated TNTAs.

Fig S4. Mott-Schottky plots of the hydrogenated TNTAs recorded at 10 Hz – 10 kHz

Fig. S5. Mott-Schottky plots of the hydrogenated TNTAs recorded at 10 kHz