Aminated TiO$_2$ nanotubes as a photoelectrochemical water splitting photoanode

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Abstract

The present work reports on the enhancement of TiO$_2$ nanotubes photoelectrochemical water splitting rate by decorating the nanostructure with an amine layer in a hydrothermal process using diethylenetriamine (DETA). The aminated TiO$_2$ tubes show a stable improvement of the photoresponse in both UV and visible light spectrum and under optimized hydrothermal conditions, 4-fold increase of the photoelectrochemical water splitting rate is observed. From intensity modulated photocurrent spectroscopy (IMPS) and electrochemical impedance spectroscopy measurements (EIS), enhanced charge transfer is observed indicating a higher charge carrier density effect of the N-doping.

Keywords: TiO$_2$ nanotubes, Diethylenetriamine, Photoanode, IMPS, Water Splitting

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1. Introduction

Since the first report by Fujishima and Honda [1] on the photoelectrolysis of water into H₂ and O₂ on a TiO₂ electrode, intensive research has been devoted to hydrogen production from water on TiO₂ photoanodes [2–6]. In photoelectrochemical water splitting on a semiconductor photoanode, conduction band electrons are transferred to a counter electrode (typically Pt) to reduce water to H₂ and valence band holes are used to oxidize water [7]. There are three key factors influencing the photoelectrolysis reaction: (1) light absorption and carrier excitation (electron-hole formation), (2) charge separation and (3) charge transfer [7]. TiO₂ remains still one of the most investigated photocatalytic material, as it is stable against photocorrosion, cost efficient and can be nanostructured.

One-dimensional TiO₂ nanoarchitectures, as nanotubes or nanowires, grant unidirectional pathways for photoexcited charge carriers and can diminish electron-hole recombination pathways [8,9]. TiO₂ being a wide band gap semiconductor (3-3.2 eV) is only able to produce photocurrent in the UV range, and only able to make use of less than 5 percent of the solar spectrum [1,2,6,9]. To improve the visible light response, extensive research was dedicated to band-gap engineering (doping) of TiO₂ using a wide range of transition metals such as Fe, Cr, Cu, and Nb, or nonmetals as C, N and S [10–19] – for an overview see ref [20].

From the available dopant materials, N-doping is used for varying the optical and electrical properties of TiO₂, and can be achieved by various techniques such as powder metallurgy, wet processes or annealing in ammonia media [21–26]. At low to medium nitrogen concentrations in the TiO₂ lattice, most reports describe the formation of N-substitutional states close to the valence band of TiO₂ [21–25], successfully narrowing the optical absorption edge and causing the well-established activation of TiO₂ in the visible range [23–25]. From the variety of doping methods, annealing of TiO₂ nanostructures in NH₃ atmosphere is one of the simplest methods for nitrogen doping of anodic TiO₂ nanotubes [27,28]. Despite the advantages
of nitrogen doping, increasing the nitrogen content in the TiO$_2$ lattice usually causes a decrease of the overall quantum efficiency due to increasing electron-hole recombination site [29,30].

Literature data already shows that amines can be adsorbed on TiO$_2$ [31], and that this adsorbed nitrogen species affect the visible light photoresponse of TiO$_2$ powders [32–34], but there is hardly any information regarding the interaction of amines decorated on nanotubular TiO$_2$ and their effect on the photoelectrochemical response.

The present study reports on the synthesis of aminated TiO$_2$ nanotube by a hydrothermal treatment of anodic TiO$_2$ nanotubes in diethylenetriamine. The quantity of the adsorbed amine depends on the temperature and time of the hydrothermal treatment, and for these aminated structures an increase of the photoresponse in both UV and visible range of light spectrum is observed.

2. Experimental

2.1 Electrochemical anodization

Titanium foils (0.125 mm thickness, 99.6% purity, Advent Research Materials) were cleaned by sonication in acetone, ethanol and deionized water, followed by drying in N$_2$ gas flow. The TiO$_2$ nanotubes were formed by anodizing 1.5 x 1.5 cm Ti foil in a 1 cm$^2$ O-ring cell, in ethylene glycol electrolyte containing NH$_4$F 0.15 M and 3 wt% H$_2$O, at 60 V for 17 min [35]. The DC potential was applied by using a power supply. Right after the anodization, the samples were immersed in ethanol for 3 hour (to remove the remnants from the organic electrolyte), and then dried under a N$_2$ gas flow. Then, the nanotubes were annealed at 450 °C in air for 1 h using a Rapid Thermal Annealer, with a heating and cooling rate of 30 °C min$^{-1}$.

2.2 Hydrothermal treatment of the TiO$_2$ nanotubes
After annealing, the nanotubular samples were immersed into an autoclave (vol. 200 ml) containing pure diethylenetriamine (SigmaAldrich; vol. 100 ml), and then heated in an oven at different temperatures (e.g. 150°C, 200°C or 250°C) for 6 h up to 18 h. Afterwards, samples were washed by distilled water (DI) water and dried in a nitrogen flow. The duration of the hydrothermal treatment was optimized in regard of obtaining a maximum photocurrent in visible region of light spectrum. Namely, various times were investigated starting from 6h up to 18h and at 12h a plateau of maximum photocurrent in visible region of light spectrum (390-600 nm) was reached – thus, the time of 12h was considered optimal for the hydrothermal treatment.

2.3 Morphological, structural and chemical characterization

A field-emission scanning electron microscope (FE-SEM, Hitachi S4800) was used to characterize the morphology of the nanotubular samples. The crystallinity of the samples was analyzed by X-ray diffraction (XRD) performed with a X’pert Philips MPD (equipped with a Panalytical X’celerator detector and using graphite monochromized Cu Kα radiation (λ = 1.54056 Å)).

The composition and the chemical state of the bare and aminated TiO₂ nanotubes were characterized using X-ray photoelectron spectroscopy (XPS, PHI 5600, US), and the spectra were shifted in relation to the Ti2p signal at 458.2 eV (the N1s, C1s and O1s peaks were fitted with the Multipak software).

In order to further investigate the amine presence of TiO₂ nanostructures, time-of-flight secondary ion mass spectrometry (TOF-SIMS) surface spectra in positive and negative polarity were recorded on a TOF SIMS 5 instrument (ION-TOF, Münster, Germany). Signals were identified according to their isotopic pattern as well as exact mass. Spectra were calibrated to
CH$_2^-$, C$_2^-$, CN$^-$ and CNO$^-$ (negative polarity) and C$^+$, CH$_3^+$, CH$_2^+$, CH$_3^+$ and C$_7$H$_7^+$ (positive polarity) and Poisson correction was employed.

2.4 Incident photon to current conversion efficiency (IPCE)

Photoelectrochemical characterization was carried out with a setup consisting of a 150 W Xe arc lamp (LOT-Oriel Instruments) as the irradiation source and a Cornerstone motorized 1/8 m monochromator. Photocurrent spectra were acquired in 0.1 M (Na$_2$SO$_4$) at a potential of 500 mV (vs. Ag/AgCl). Photocurrent spectra were measured in a three-electrode configuration, consisting of 1 cm$^2$ TiO$_2$ nanotubes as photoanode area, platinum wire as a counter electrode and an Ag/AgCl (3 M KCl) electrode as a reference by a JAISSLE IMP 83 PCT-BC Poentiostat-Galvanostat. The electrochemical cell was adjusted horizontally in front of the light source. IPCE for each wavelength was calculated according to (Eq. (1) and (2)):

$$IPCE(\%) = \frac{I_{ph} \times h\nu}{p \times q} \times 100$$  \hspace{1cm} (1)

$$I_{ph} = I_{on} - I_{off}$$  \hspace{1cm} (2)

where $I_{on}$ is steady-state current after light illumination in each wavelength, $I_{off}$ is steady-state current after light illumination in each wavelength, $I_{ph}$ is photocurrent density, $P$ is the power density of light, $h\nu$ ($\approx$1240) photon energy of the incident light, $q$ charge of the electron.

2.5 Intensity modulated photocurrent spectroscopy (IMPS)

Intensity modulated photocurrent spectroscopy (IMPS) measurements were carried out using a Zahner IM6 (Zahner Elektrik, Kronach, Germany) with a tunable TLS03 UV and Visible light source. The photoelectrochemical performance of the samples was analyzed in aqueous 0.1 M Na$_2$SO$_4$ solution in a three-electrode configuration, consisting of 1 cm$^2$ TiO$_2$ nanotubes as photoanode area, platinum wire as a counter electrode and an Ag/AgCl (3 M KCl) electrode as a reference.
During IMPS, the potential of samples is potentiostatically controlled and set to 0 V (short-circuit conditions). The generated photocurrent is measured. At short-circuit conditions, the band gap between non-conductive valence band and conduction band of the semiconductor is maximum. As a result, nearly no electrons are injected into the conduction band. Most reactions occur on the back layer of the anode and electrons are migrating from the location where they are generated to the electrode’s back layer. The electrochemical impedance measurements were done under modulated light ($\lambda = 369$ nm & 475 nm) and Nyquist plots were measured. The curves show a maximum at intermediate frequencies. This point is characteristic for the electron transport through the pores of the anode to the back layer. The corresponding electron transport time constants were evaluated by IMPS. The technique exhibits a specific frequency $f_{IMPS}$ which is inversely proportional to electron transport time ($t_{tr}$) according to Equation 3.

$$t_{tr} = \frac{1}{2\pi f_{IMVS}}$$  

(3)

### 2.6 Photoelectrochemical water splitting

The photoelectrochemical water splitting experiments were performed under simulated AM 1.5G illumination (100 mW cm$^{-2}$) supported by a solar simulator, in 1M KOH aqueous solution. A three-electrode configuration was used in the measurement, with the TiO$_2$ nanotubes (before – bare, and after hydrothermal treatment – amination) as a working electrode (photoanode), Ag/AgCl as a reference electrode, and a platinum foil as a counter electrode. The cell was adjusted vertically under the light source to ensure the specified power. Photocurrent versus voltage curves were acquired by scanning the potential from −0.5 to 0.7 V with a scan rate of 1 mV.s$^{-1}$ using a Jaissle IMP 88 PC potentiostat. The stability measurements were performed at 0.5 V (vs. Ag/AgCl) in 1 M KOH for 1 hour.
Photocurrent transient of bare and aminated TiO$_2$ nanotube were measured under monochromatic (474 nm) 20 mW laser illumination. A three-electrode configuration was used in the measurement, with the TiO$_2$ nanotubes (before – bare, and after hydrothermal treatment – amination) as a working electrode (photoanode), Ag/AgCl as a reference electrode, and a platinum foil as a counter electrode.

### 2.7 Electrochemical impedance spectroscopy and cyclic voltammetry

Cyclic voltammetry was conducted at a constant scan rate of 100 mV/s, scanning range of 0-1 V in 0.1 M Na$_2$SO$_4$. Before each experiment, the working electrode was immersed for 40 min in the test cell until open circuit potential reached a steady state condition. All tests were carried out at 25°C (within ±1 °C) made possible by using a water bath to control the cell temperature.

Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 100 kHz to 10 mHz with the amplitude of 10 mV peak-to-peak using AC signals at OCP. Electrochemical tests were conducted by means of Zahner IM6 (Zahner Elektrik, Kronach, Germany). The curves were fitted with Zfit-EC-Lab 10.44 spectrum analyzer (simplex method).

### 3. Result and Discussion

Previous reports [16,36] have indicated that for photoelectrochemical water-splitting of anodic nanotubular layers, there is an optimal thickness of the nanotubular layers allowing full-light absorption and minimized electron-hole recombination of ≈ 7 µm. Hence, this length range of the TiO$_2$ nanotubes was used in the present work. After anodization, the nanotubular samples were annealed at 450°C in order to convert the amorphous structure to a crystalline one (anatase). The obtained crystalline TiO$_2$ nanotubes (NTs) are shown in Figure 1 a-c and the nanotubes present a typical morphology for NTs obtained in organic electrolytes [8,37], i.e.,
well-defined nanotubular layers with a tube diameter of \( \approx 100\text{nm} \), a length of \( \approx 6.5 \mu\text{m} \) smooth and ripple-free nanotube walls and a double-walled structure.

It is known that for compact or nanoparticulate TiO\(_2\) [31,33,38], amino groups can adsorb and influence the visible light photoresponse. For the synthesis of aminated nanoparticulate TiO\(_2\), amines are usually added directly in the hydrothermal synthesis. However, the hydrothermal treatment of TiO\(_2\) nanotubes is more delicate (e.g. decay of the nanotubular structure), therefore it is not surprising that amine treatments on TiO\(_2\) nanotubes have not been reported. Herein, an amino group containing layer was coated on the TiO\(_2\) NTs by a hydrothermal treatment performed in diethylenetriamine (DETA) and was carried out at different temperatures (150°C, 200°C or 250°C) for 12h. Diethylenetriamine (C\(_4\)H\(_{13}\)N\(_3\)) was used, as it presents a higher nitrogen to carbon ratio (0.75) compared to other amines, e.g. dimethylamine ((CH\(_3\))\(_2\)NH), ethylamine (C\(_2\)H\(_7\)N) etc.

For all aminated TiO\(_2\) NTs samples, no difference in the morphology of the nanotubes compared to the bare TiO\(_2\) nanotubes was observed, e.g. comparative SEM images of the bare and aminated NTs (at 250°C) are shown in Figure 1 (d-f vs a-c) – data not shown for 150°C and 200°C. There is no visual or morphological alteration apparent from SEM images that would indicate any film formation on the nanotubes or on the tube tops after the hydrothermal treatment in DETA.

The as-formed TiO\(_2\) nanotubes are amorphous and are annealed to anatase, thus showing the peaks corresponding to anatase, A, and to the substrate (Figure 1.g). The hydrothermal treatment had no influence on the crystallinity of the anatase NTs layers, as observed by XRD i.e. there is no significant difference of patterns between the bare (anatase TiO\(_2\) nanotubes) and aminated NTs (hydrothermal treatment at 250°C – Figure 1.h); similar XRD data were obtained for 150°C and 200°C, data not shown.

To confirm the presence of the amino group on the nanotubular samples after the hydrothermal treatment, high resolution XPS spectra of N1s, C1s, Ti2p and O1s were
performed and as seen from Figure 2, an increase in the N1s and C1s peaks is observed, while no significant difference is observed for Ti2p and O1s (data not shown for O1s at 530 eV). Additionally, the homogeneity of the samples was confirmed by XPS top measurements in 5 different spots on the 250°C aminated nanotubes (similar spectra and percentages were obtained). From the N1s spectra, the presence of nitrogen is clearly detected for all aminated samples (150°C, 200°C and 250°C), i.e. the N1s peak at approximately 399.8 eV that results in higher N at.% compared to the bare TiO₂ nanotubes (that contain low amount of N due to pick up from the environment), see Figure 2.b and Table 1. In the C1s spectra, an increase in the C peaks is observed for all aminated NTs (Figure 2.b and Table 1), due to the presence of C-N and C-C bonds in the DETA [31]. The 4.2 at.% C content in the bare TiO₂ NTs (annealed to anatase and not subjected to an amination treatment) is due to the adventitious carbon contamination and to remnants from the organic electrolyte in which the nanotubes were grown (the remnants from the organic electrolytes are partly burned off during the conversion of tubes from amorphous to anatase) [8, 39]. Moreover, for all aminated samples we observe a shift of the C1s peak to approximately 286.2 eV, which is due to the C-N bonds (≈286 eV); also, for the 250°C aminated NTs, there is a shoulder at higher binding energies (288-290 eV) which can be ascribed to the presence of both amide carbon (N-C=O, ≈287.8 eV) or carbon in carbonates (O=C-OH, ≈288.5 eV). These data can confirm the decomposition of DETA during the hydrothermal treatment and the possibility of amino group adsorption on the surface or doping nitrogen in the TiO₂ lattice. To emphasize the effect of the thermal amination, NTs that were immersed at room temperature in DETA (adsorbed RT) were also characterized: in this case only very little amine is adsorbed on the TiO₂ surface, as there are no significant difference in the N at.% compared to the bare NTs, however in the C1s spectra a small peak corresponding to C-N bonds at approximately 286.2 eV is observed.

Additionally, in order to distinguish between the chemical states of the nitrogen in the aminated samples, the N1s peak was deconvoluted (e.g. 250°C aminated NTs in Figure 2.d) and the fitting resulted into three peaks at 398.6 eV – assigned to amino groups bonded to the
TiO$_2$ surface, 399.6 eV – to nitrogen doped in the interstitial lattice condition, and at 401.5 eV corresponding to protonated amines or oxidized N species [40,41]. This is consistent with literature data, previous work by Farfan-Arribas et al. [31] on amine adsorption and that of Beranek and Hirsch [42,43] on thermal treatment of TiO$_2$ nanoparticles in urea. The deconvolution results for all aminated samples are listed in Table 1 and with increasing the temperature of the hydrothermal treatment there is an increase in the amount of doped nitrogen and also in the amount of N bonded to the TiO$_2$ surface (after deconvolution).

Selected signals from ToF-SIMS surface profiles are presented in Figure 3 and these correspond to the following selected characteristic fragments in positive polarity: TiO$^+$ (mass 63.94), C$_2$H$_6$N$^+$ (mass 44.05), C$_3$H$_7$N$_2$O$_2^+$ (mass 103.05) and while no difference in observed in the fragments corresponding to the TiO$_2$ nanotubes (i.e. TiO$^+$, and also for Ti$^+$), an increase is detected for fragments of the DETA (e.g. C$_2$H$_6$N$^+$, C$_3$H$_7$N$_2$O$_2^+$ and also for other fragments such as C$_2$H$_2$N$^+$, C$_3$H$_6$NO$^+$, C$_2$H$_7$N$_2^+$ for which data is not shown here). Moreover, in negative polarity an increase is observed also in fragments such as CN$^-$ (mass 26.00) or CHN$^-$ (mass 27.00). ToF-SIMS surface profile data are correlating with the XPS data, confirming the presence of amino groups on the TiO$_2$ nanotubes surface.

The photocurrent spectra of differently treated NTs layers are shown in Figure 4a, i.e. bare nanotube layers (as-grown and converted to anatase), hydrothermally treated NTs in DETA (aminated layers at 150°C, 200°C or 250°C) and for DETA adsorbed NTs at room temperature (25°C). The highest photocurrent density is achieved for aminated nanotubes at 250°C, followed by the amination at 200°C and 150°C, respectively. DETA adsorbed at room temperature on the TiO$_2$ NTs does not induce any change in the photocurrent spectra, in addition XPS data indicated no significant amine adsorption compared to the bare NTs, in these conditions. From Figure 4a one can see that amination (i.e. hydrothermal treatment in DETA) increases not only the visible photo response but also the photocurrent response in the UV region. In previously published N-doping research [30], N-doping led to a significant decrease
in quantum efficiency at the UV region of the solar spectrum and further increasing the nitrogen content caused a decrease of quantum efficiency in both UV and visible region of solar spectrum, as a result of increasing electron-hole recombination sites (traps) [29]. The incident photon to current efficiency (IPCE) reaches values of 7-19% at the UV spectrum maximum and values of 0-3.5% at the visible spectrum (Figure 4c) supporting that the aminated nanotubes show an increased quantum efficiency in both UV and visible range (due to increasing amount of adsorbed nitrogen species).

Figure 4b presents the $(I_{ph \text{ norm } h\nu})^{0.5}$ vs. $h\nu$ plots, from which the band gap ($E_g$) values can be evaluated. The photoresponse for untreated TiO$_2$ nanotubes (i.e. non-doped TiO$_2$ nanotubes in the form of anatase) is in line with previous work [8] and shows the expected $E_g$ values for anatase at 3.15 eV. However, the significant increase in the magnitude of the photocurrent in the visible region can be related to formation of sub-band gaps with much lower values, i.e. with the value of $\approx 2.2$eV for the 250°C aminated TiO$_2$ NTs. Hence, this can be due to the adsorption of nitrogen containing species on the surface of TiO$_2$ nanotubes that could result in a sub band gap of N2p between O2p and Ti3d state [29,44]. The optimal hydrothermal time was of 12 h (see Figure 4d and experimental section).

Intensity modulated photocurrent spectra (IMPS) for the bare and 250 °C aminated nanotubes are shown in Figure 4e for monochromatic 369 and 475 nm light illumination, and faster electron transport times are observed for the aminated NTs. Results under UV illumination clearly show that essentially the same power-law dependence on the incident light intensity and lower transport time is in aminated sample. Such power-law dependence is normally attributed to the nature of the trap distribution [45–47]. A recent study [48] shows that the traps limiting transport in TiO$_2$ nanoparticle films are located predominantly on the surface of the oxide. Hence, the shift in transport time occurs due to the decreasing of trap sites at the surface and one can say that the hydrothermal treatment can decrease the number of traps on the surface and thus causing the increase in the UV response, in the IPCE spectrum. The
difference between the transport times coefficient can also indicate that the aminated NTs show a power-law dependence, however a different intensity does not such a definite impact in the case of the bare anatase TiO$_2$ nanotubes.

The aminated TiO$_2$ nanotubes were further evaluated for photoelectrochemical water splitting under simulated sunlight conditions (AM 1.5 at 100mWcm$^{-2}$) – see Figure 5a. From the transient-photocurrent versus potential curves, it is evident that with amination of the TiO$_2$ nanotubular samples the photocurrent density is significantly enhanced. Furthermore, there is a correlation between the temperature of the hydrothermal treatment, namely the temperature at which the amination is performed, and the increase in the photocurrent density. We observed that a higher temperature of the hydrothermal treatment results in increasing adsorbed amino group species on the TiO$_2$ surface and doped nitrogen in TiO$_2$ lattice those results in an improvement of their photoelectrochemical properties. The photocurrent density of the 250 ºC aminated TiO$_2$ NTs presents a 4-fold increase compared to the bare TiO$_2$ nanotubes (anatase). In addition, the aminated layers present a good photostability over 1h – see Figure 5b.

The photocurrent transients of bare and 250 ºC aminated TiO$_2$ nanotube and under monochromatic laser ($\lambda = 474$ nm) are shown in Figure 5c, and the long-term (24h) PEC experiment (Figure 5d) confirms the stability of these layers (the amount of N did not significantly drop after the long-term tests). These data are consistent with the photocurrent response of aminated NTs in visible light and further corroborate the IPCE measurement (Figure 4). However, the photocurrent transient registered for the bare NTs has negligible values and can be due to the presence of remnant carbon species in the nanotubes (i.e. from the carbon inner layer of the classical double-walled nanotubular structure) [8,44]; generally, this absorption feature is of a broadband nature, namely it extends up to ca. 600 nm [49]. Recent work [49] points out that such a small current response for anatase TiO$_2$ nanotubes can be attributed to a photo sensitization of the carbon layer in the nanotubes. Moreover, our results are consistent with the classic amination process of TiO$_2$ nanoparticles by thermal treatment
with urea vapors [42,43] and the increased visible light absorption is explained in terms of surface states.

The results of the impedance measurements (EIS) are shown in Figure 6 and Table 2. The nanotube layers are composed of an outer tube layer and an inner barrier layer. The spectra obtained for titanium with nanotube layers were interpreted by using a model with two constants. The equivalent circuit is shown in Fig. 6c and the components of this equivalent circuit are the electrolyte resistance ($R_s$), resistance of the outer tube layer ($R_{out}$), CPE of the outer tube layer ($P_{out}$), resistance of the inter layer ($R_{in}$) and CPE of the inter-barrier layer ($P_{in}$).

Figure 6 presents the representative electrochemical impedance data for Bode and Nyquist diagrams and the fitted points obtained with the simulation of the model. The chi-square values of $10^{-3}$ for nanotube layers indicate excellent fit quality between the simulated and measured data. Results indicate significantly improved electrode conductivity with lower charge transfer resistance after amination. Increasing the capacitance and decreasing the resistance of both inner and outer layer can be related to increasing the defects, which are responsible for electron transfer inside the nanotube due to nitrogen doping; supporting the increased electron transfer coefficient after amination (IMPS measurements). In addition, Figure 6d presents the cyclic voltammetry data.

Literature reports on PEC performance of modified TiO$_2$ nanotubes shows that nitrogen doping increases the performance, e.g. Tong et al. [50] – three time increase in PEC performance of a reduced TiO$_2$ nanotstructure (by using a nitrogen-doped carbon film), and Wu & Zhang [51] showed a 5-time enhancement in double-walled nitrogen doped TiO$_2$ nanotube structure. In comparison, almost similar PEC and nitrogen concentration can be achieved, however due to the formation of transition metal complexes in DETA [52], there is the possibility of co-doping and decoration; thus, it is plausible that such treatments can be transferred to other state-of-the art nanotubular structures (higher surface area, less contaminated, etc.) or to other TiO$_2$ nanostructures.
Conclusions

In summary, the present work shows that aminated TiO$_2$ nanotubular structures (via hydrothermal treatment of anodic TiO$_2$ nanotubes in diethylenediamine) represent a straightforward method for increasing the photoelectrochemical response of nanotubes. The amination of the nanotubular structure does not modify its morphology or crystal structure; however, it leads to a decoration of the tube with an amino group containing layer and interstitial nitrogen doping of TiO$_2$. This leads to an increase in the photocurrents for both UV and visible regions of the light spectrum. Compared to bare TiO$_2$ nanotubes, under optimized conditions, aminated TiO$_2$ nanotubes (after a hydrothermal treatment at 250 ºC) result in a 4-fold increase of the water splitting current density and this effect is stable with illumination time. Combining the amination treatment with other doping methods for TiO$_2$ nanotubes or with higher quality nanostructures (higher surface area, less contaminated oxide) may result in further improvement of the photoelectrochemistry.

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Figures and table captions

Figure 1: a,b and c) Top and cross-section view SEM images of bare TiO2 nanotubes; d, e and f) hydrothermally treated nanotube in DETA at 250°C; g) XRD of bare TiO2 nanotubes and of h) hydrothermally treated nanotubes in DETA.

Figure 2: a) N1s, b) C1s and c) Ti2p high resolution XPS spectra for bare TiO2 nanotubes (bare NTs), hydrothermally treated NTs (at 150°C, 200°C and 250°C) and for DETA adsorbed at room temperature (adsorbed RT). d) Deconvolution of the N1s peak for the 250°C aminated TiO2 nanotubes.

Figure 3: Selected fragments from the ToF-SIMS surface profiles of bare TiO2 nanotubes (NTs) and 250°C aminated nanotubes (250°C) in positive polarity – TiO+ (m/z 63.94), C2H6N+ (m/z 44.05) and C3H7N2O2+ (m/z 103.05); and in negative polarity – CN− (m/z 26.00), CHN− (m/z 27.00).

Figure 4: a) Photocurrent spectra of the TiO2 nanotube before and after hydrothermal treatment at different temperature in DETA; b) Evaluation of the band gap-energy of the samples from a); c) IPCE spectra of the TiO2 nanotube before and after hydrothermal treatment at different temperature in DETA d) Influence of the hydrothermal treatment time on the photocurrent spectra of the TiO2 nanotube aminated at 250°C; e) Comparison of transport time constants for bare and aminated TiO2 nanotube as a function of the incident photon flux, for monochromatic 369 and 475 nm light illumination;

Figure 5: a) Photocurrent transient vs potential curves of different hydrothermal treatment at different temperature in DETA; b) corresponding photostability experiment for 1 h at 500 mV; c) Photocurrent transient under monochromatic laser (λ = 474 nm) for the 250°C aminated nanotubes. d) Long-term photostability experiment for 1 h at 500 mV for the TiO2 nanotubes aminated at 250 °C in DETA.
Figure 6: a) Bode and b) Nyquist plots of electrochemical impedance measurements of bare and aminated TiO\textsubscript{2} nanotubes in 0.1 M Na\textsubscript{2}SO\textsubscript{4} e) equivalent circuit for TiO\textsubscript{2} nanotube structure d) cyclic voltammetry curve of bare and aminated TiO\textsubscript{2} nanotubes in 0.1 M Na\textsubscript{2}SO\textsubscript{4}

Table 1: The chemical composition (at.\%) of the bare and aminated TiO\textsubscript{2} nanotubes computed from XPS data.

Table 2: Impedance data for bare and aminated TiO\textsubscript{2} nanotubes at 250°C.

Table 1

| Sample                        | C (at.\%) | N (at.\%) | O (at.\%) | Ti (at.\%) |
|-------------------------------|-----------|-----------|-----------|------------|
| Bare TiO\textsubscript{2} NTs | 4.2       | 0.5       | 67.5      | 27.8       |
| Aminated TiO\textsubscript{2} nanotubes |           |           |           |            |
| 150°C                         | 9.4       | 1.1       | 64.9      | 24.6       |
| 200°C                         | 10.0      | 1.7       | 63.8      | 24.5       |
| 250°C                         | 10.6      | 2.2       | 64.0      | 23.2       |
| DETA adsorbed at room temperature (Adsorbed RT) | 2.5 | 0.5 | 68.8 | 28.2 |

Table 2

| Deconvolution of the N1s peak for aminated TiO\textsubscript{2} nanotubes | Bonded to TiO\textsubscript{2} surface, at.\% | Doped N, at.\% | Protonated amine, at.\% |
|-------------------------------------------------|-----------------|----------------|----------------------|
| 150°C                                           | 0.62            | 0.46           | 0.20                 |
| 200°C                                           | 0.90            | 0.66           | 0.14                 |
| 250°C                                           | 0.61            | 1.24           | 0.35                 |
| Sample                  | $R_s$ (Ω.cm$^2$) | $R_{out}$ (KΩ.cm$^2$) | CPE$_{out}$ | $R_{in}$ (KΩ.cm$^2$) | CPE$_{in}$ | $P_{out}$ (μF/cm$^2$) | $a_{out}$ | $P_{in}$ (μF/cm$^2$) | $a_{in}$ |
|------------------------|-----------------|-----------------------|-------------|----------------------|-------------|-----------------------|----------|----------------------|---------|
| TiO$_2$ NTs            | 22              | 24.6                  | 5.9         | 0.92                 | 2.5         | 57.9                  | 0.91     |                      |         |
| 250°C aminated TiO$_2$ NTs | 24              | 16.7                  | 472         | 0.95                 | 0.7         | 645                   | 0.72     |                      |         |

**Figure 1**

- **a)**
- **b)**
- **c)**
- **d)**
- **e)**
- **f)**

**A** : Anatase
**T** : Ti

**20**  **30**  **40**  **50**  **60**  **70**  **80**

**Intensity (a.u.)**
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6