Optimized spacing between TiO₂ nanotubes for enhanced light harvesting and charge transfer

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link to the published article:

<https://onlinelibrary.wiley.com/doi/full/10.1002/celc.201801136>

Abstract: In the present work, we investigate two distinctly different anodic TiO₂ nanotubular morphologies, spaced and close-packed arrays. While the close-packed tubular arrays are formed in ethylene glycol, spaced NTs, which have a regular gap between individual nanotubes, grow in a diethylene glycol or dimethyl sulfoxide based electrolyte. Depending on the electrolyte used for anodization, the morphology, crystal structure and chemical composition of the resulting nanotubular layer vary from one another. This influences the electrochemical and photoelectrochemical activity of nanotubes. Overall, we find that spaced NTs not only can provide enhanced charge transfer characteristics but also can show beneficial light absorption characteristics when used as a photo or light harvesting electrode.

Introduction

Since the first reports on self-ordered nanotube or nanopore growth on Ti or Ti alloys through electrochemical anodization by Assefpour-Dezfuly et al.^[1] and later by Zwilling et al.,^[2] Gong et al.^[3] and Beranek et al.,^[4] TiO₂ nanotubes (NTs) have been explored for a broad range of applications and have become one of the most investigated nanostructures over the past decade.^[5]

Meanwhile, a high level of control over morphological features, such as diameter, length, wall thickness, wall structure, as well as over crystallinity (amorphous, anatase, rutile) has been achieved.^[5,6] A range of morphological variations has been produced, including bamboo tubes, branched tubes, the fabrication of membranes, or single-walled TiO₂ NTs.^[5,7–10]

Generally, self-ordered TiO₂ nanotube arrays grow in a hexagonally close-packed (CP) configuration, i.e., have no or only a very narrow tube-to-tube spacing (top spacing). However, previous works show that with a certain electrolyte composition, spaced (SP) NTs having a regular gap between individual tubes are obtained.^[11–14] In particular, SP NTs grow in the electrolyte that contains diethylene glycol (DEG) or dimethyl sulfoxide (DMSO) as organic solvents (in addition to HF and H₂O). Also some other solvents, e.g., ethylene glycol (EG), tri(tetra, poly)-ethylene glycol were reported, that can promote the growth of spaced or “loose-packed” NTs – this always under a specific set of anodization conditions^[15,16] and are responsible for establishing the regular tube-to-tube spacing.

A general advantage of all vertically aligned nanotubes grown by anodic oxidation is that they offer a direct electron pathway to a back contact (in contrast to particle-like nanostructures). Therefore, throughout the past decades, TiO₂ nanotubes, specifically conventional CP TiO₂ nanotubes, have been extensively studied for a wide range of applications where this direct electrode contact is beneficial, such as dye-sensitized solar cells,^[17,18] fuel cells,^[19,20] Li-ion batteries,^[21,22] photocatalysts,^[23,24] bio-applications^[25,26] and sensors.^[27] As SP NTs have been only recently introduced, relatively little is known about their properties – particularly their photoelectrochemical properties, in comparison to conventional close-packed tubes.

In general, morphological features of TiO₂ nanotubes, e.g., tube diameter, wall structure (double- versus single-walled), wall thickness, and length of NTs affect the electrochemical and photoelectrochemical activity by influencing the total surface area, electrolyte diffusion, light reflection and light absorption of oxide.^[5,28–30] The photoresponse of tubular layers is usually determined by two main phenomena: i) absorption of light and generation of electron-hole pairs,

versus ii) the recombination of the electron-hole pairs.^[29,31–33] For many TiO₂ nanotube layers used in the UV-Vis (solar spectral) range, an optimum length typically is some μm for a most efficient photoconversion in aqueous electrolytes.^[29,34] Also, the tube diameter influences the photoelectrochemical behavior of NTs; small diameter NTs (mainly in the form of anatase) are reported to be photoelectrochemically more active due to the higher diameter-dependent population of photo-generated electrons.^[30] Another important characteristic is the crystallinity of nanotubes. Non-crystalline (amorphous) or partially crystalline TiO₂ NTs exhibit limited/low or no activity due to the disordered, defective structure.^[35,36] On the other hand, NTs composed of anatase demonstrate a higher electron mobility and electrical conductivity than anatase-rutile mixtures or rutile phase.^[35,37,38] In the case of spacing, previous work investigated the influence of spacing and nanostructure density on light harvesting using TiO₂ nanorods and concluded that an optimal rod density (spacing) yields enhanced light harvesting.^[39] However, up to now, in literature, there is hardly any investigation on the influence of interspacing of TiO₂ nanotubes (tube-to-tube spacing) on light absorption and charge transfer characteristics.

Therefore, in the present work, we evaluate the electrochemical and photoelectrochemical activity of spaced TiO₂ nanotubes and compare it with a close-packed morphology. We find that the spaced tubes provide some specific beneficial features in photoelectrochemical applications.

Results and Discussion

Figure 1 a–c shows the top, cross-section and bottom view SEM images of EG, DEG and DMSO based tubular layers with a thickness of 3 μm . The EG CP NTs are composed of tightly arranged NTs, different from the loosely-packed SP tubular arrays where the spacing is filled with secondary smaller size NTs, see previous reports.^[40,41] To illustrate, Figure 1b2 and c2 exhibit SEM images of the nanotubes from bottom and cracked-off close to the bottom (small and large diameter nanotubes are highlighted), clearly showing that large diameter NTs are surrounded by smaller size nanotubes.

Figure 1. SEM images show: EG based close-packed TiO_2 NTs with a1) top view (inset demonstrates the cross-section view) and a2) bottom view. DMSO based spaced TiO_2 NTs with: b1) top view (inset demonstrates the cross-section view) and b2) bottom view. DEG based spaced TiO_2 NTs with c1) top view (inset demonstrates the cross-section view) and c2) cracked-off NTs close to tube bottom.

The geometrical features of tubes are summarized (see Figure S1) as follows: the outer diameter of EG, DMSO and DEG NTs are 81 ± 5 nm, 127.5 ± 9 nm and 169 ± 17 nm, respectively. The spacing (tube-to-tube) between NTs is 150 nm for DEG and 139 nm for DMSO based NTs.

The space initiation alters the tube density, namely, the SP NTs have one to two orders of magnitude less nanotube per cm^2 than CP NTs, therefore, SP NTs have less active surface area in comparison with CP NTs. This might be the reason for the lower electrochemical activity of bare SP NTs.^[42,43] Another morphological difference between these tubular arrays is the wall structure; for instance, while EG (from tube top to tube bottom) and DEG NTs (only close to the tube bottom) show a double-walled morphology, DMSO based tubes have a single-walled structure.^[41,44]

Figure 2. SEM images of ion-milled NTs close to tube bottom view show a) EG based close-packed NTs, b) DMSO based spaced NTs, and c) DEG based spaced NTs (inset views show a single nanotube, scale bars are 100 nm). Scale bars are 200 nm.

Figure 2 a-c illustrates ion-milled cross-sections of as-formed tubular layers and an inset with a high magnification image of a single tube. While the CP NTs exhibit a uniform size distribution, SP NTs are surrounded by smaller size tubes. The morphology of small diameter tubes varies depending on the electrolyte; while DEG based nanotubes have properly formed small diameter tubes, over-etched small diameter nanotubes are evident in the case of DMSO based SP NTs. This phenomenon can be ascribed to the fact that the DEG spaced nanotubes exhibit a slow growth rate (at room temperature) in comparison with SP NTs prepared in DMSO electrolyte (at 30 °C); namely, the fast growth rate is responsible for the over-etched small diameter nanotubes. Moreover, nanotubes are embedded in a fluoride-rich layer, and the thickness of the fluoride-rich layer as well as of the barrier layer differs from one another. As an illustration of this fact, the barrier layer of EG CP and DMSO SP NTs is 46 nm; differently, DEG NTs have the thickest barrier layer with 52 nm. On the other hand, EG CP NTs have a thicker fluoride-rich layer (26 nm) than SP NTs (11-13 nm). It is expected that these features, the wall structure, as well as the thickness of the barrier and fluoride-rich layer, will influence the charge transfer behavior (resistance) of nanotubular arrays. For instance, it is reported that the fluoride-rich layer weakens the mechanical and chemical stability of NTs and causes the delamination of the tubular layer,^[44,45] which can lead to the poor electrical conductivity. Another difference between tubular layers is in the topology of tube bottoms: while spaced tube bottoms have a rough brainy-like morphology, the CP NTs show a smooth tube bottom, see Figure 1 a2 and b2.

The chemical composition and the incorporation of electrolyte species within the oxide films were evaluated by XPS analysis. Figure 3 and S2 show the comparisons of survey XPS spectra and high resolution spectra of Ti2p, O1s, C1s and F1s peaks for the three morphologies (as-formed nanotubes). Please note that no S is detected for the nanotubes obtained in DMSO electrolyte. The high resolution Ti2p spectra exhibit the characteristic peaks of TiO₂, 464.5 eV and 458.6 eV, corresponding to 2p_{1/2} and 2p_{3/2} doublet peaks (see supporting information, Figure S2a), respectively.

Figure 3. XPS analyses of EG close-packed, DMSO and DEG spaced TiO₂ nanotubes: a) survey spectra, b) C1s high resolution spectra. c) XPS depth profiles show the variation of carbon content. d) F1s high resolution spectra. e) XPS depth profiles show the variation of the fluoride content. f) X-ray diffraction patterns of as-formed and annealed EG, DEG and DMSO based nanotubular arrays (EG (1,2), DMSO (3,4), and DEG (5,6) NTs respectively: (1), (3), (5) indicate as-formed and (2), (4), (6) show annealed NTs). Note that A → anatase, R → rutile, Ti → metallic titanium.

The high resolution O1s spectra reveal that the main oxygen peak is at 530 eV indicating the bond between Ti and O, TiO₂ (see Supporting Information, Figure S2b). For tubular arrays, a widening of the oxygen peak at higher binding energy is more pronounced, and is usually

attributed to OH^- and H_2O (531-532 eV), respectively.^[46,47] In the C1s spectra, three peaks are recognized; the peak at 284.8 eV corresponds to C-C bond, at 286.8 eV identifies the C-O-C bonds and at 288.5 eV indicates the O-C=O bonds, see Figure 3b. The XPS C-depth profiles of nanotubular layers demonstrate a higher carbon content (in the top 10-20 nm of the tubular layer) of EG based nanotubes, as illustrated in Figure S3 in Supporting Information. Figure 3d shows the F1s peak and according to the spectra, DMSO and DEG SP-TiO₂ nanotubes exhibiting a stronger fluoride signal at 684-685 eV show the presence of $[\text{TiF}_6]^{-2}$, while the peak at 692 eV corresponds to C-F bonds. Different from the spaced nanotubes, EG CP-TiO₂ NTs display an additional peak at 687.7 eV that is attributed to absorbed fluorine or organic fluorine. The XPS depth profiling in Figure 3e indicates somewhat higher fluoride content for DMSO and DEG NTs, which may arise from the high F-ion concentration in the electrolytes used for anodization. Note that for the spaced tube formation, F-ions play a key role to initiate tube-to-tube spacing, see previous report.^[40] Overall, the main compositional difference between spaced and close-packed nanotubes can be summarized as follows: while EG NTs have a higher carbon content, DEG and DMSO NTs exhibit a slightly higher fluoride content (Figure S3).

We have also performed XPS analysis for the annealed nanotubular arrays, as shown in Supporting Information (Figure S3-S5). According to the spectra, Ti2p and O1s peaks confirm the presence of TiO₂ similar to as-formed NTs. Different from the as-formed NTs, the concentration of C1s and F1s drastically reduces due to the decomposition of fluoride- and carbon-rich layers during heat treatment, see Figure S3 and S5 in the Supporting Information. In line with the literature,^[44,48,49] the atomic concentration of C and F become lower throughout the tubular layers. Note that, spaced NTs show a slightly higher fluoride content, which can be due to the utilization of fluoride-rich electrolyte during anodization. Although fluorides have been reported to act as a dopant on TiO₂,^[50,51] the amount of remaining fluoride or carbon is too low to assign a critical role to the carbon or fluoride-rich layer in view of influencing the electrochemical and photoelectrochemical behavior of the annealed NTs.

In order to determine the elemental distribution throughout the tubular layer, EDX analyses were performed at three different locations of the nanotubes (top, middle and bottom) for as-formed as well as for annealed nanotubular arrays, see Figure S6 in Supporting Information. In line with the XPS analyses, crystalline nanotubular arrays show lower amount of carbon and fluoride content in comparison to the as-formed nanotubes. On the other hand, spaced NTs have a higher fluoride content and a lower carbon content throughout the nanotube thickness than close-packed NTs. The higher carbon content of EG and DEG NTs than DMSO NTs is ascribed to the double-walled morphology of nanotubes (note that for DEG NTs, the double-walled

morphology is visible only close to the tube bottom). Note that the variation between at% obtained by EDX and XPS analyses arises because of the difference in working principle of EDX and XPS. While the information depth of EDX is several micrometers, XPS gives information about the top most layer (i.e. only a few nanometers).

The morphology or the wall structure, i.e., single- vs. double-walled, affects the chemical composition of as-formed and annealed nanotubes. As such, XPS and EDX analyses (Figure S3 and S6) prove that the tubular layer with a double-walled structure (EG and DEG NTs) has a higher carbon content, which mainly comes from the carbon-rich inner shell.^[44] This is in contrast to tubes with a single-walled structure (outer shell - OS), e.g., NTs formed in DMSO electrolyte where such a carbon-rich layer is absent.^[12]

The other characteristic that influences the electrochemical and photoelectrochemical activity of NTs is crystallinity. To define the phase composition of NTs, XRD analysis was performed on the NTs annealed at 450 °C, see Figure 3f. The EG CP NTs demonstrate a stronger anatase peak, while the rutile peak is not visible. However, in the case of SP NTs, a small rutile peak at 27.5° (110) is recognizable. The phase composition is determined using Equation (1), outlined as follows: EG NTs have the highest anatase ratio with 92 % (8 % is rutile), followed by DEG (85 %) and DMSO (80 %) based NTs. It is well-known that the rutile formation starts between the oxide/metal interface in line with literature,^[52–54] therefore, it is probable that the small diameter tube stacks in the lower part of nanotubes can be easily converted into rutile leading to a higher rutile content. Accordingly, Bauer et al. showed that annealing of nanotubes with a diameter smaller than 30 nm leads to the formation of rutile rather than anatase.^[55] These findings could explain the higher rutile content of spaced nanotubular arrays.

The grain size of anatase was calculated using the Scherrer equation, Equation (2), by considering the diffraction peak of anatase (101). The calculated size of anatase grains for NTs produced in EG, DEG, and DMSO is 20 nm, 22.5 nm, and 23.4 nm, respectively. The crystallite size of SP NTs is slightly bigger than for CP NTs. It is worth to mention that there is no strong evidence showing a direct relationship between tube spacing and the grain size, which is in contrast to previous reports that the heat treatment of single-walled tubes induces a larger crystallite size.^[5]

All these morphological features, i.e., wall thickness, wall structure (double-walled versus single-walled), tube-to-tube spacing, outer diameter, nanotube density, and more importantly the crystallinity determine the electrical, optical, electrochemical and photoelectrochemical properties of nanotubular arrays.

Figure 4. Photoelectrochemical characterization of EG close-packed, DMSO and DEG spaced TiO_2 NTs: a) IPCE spectra in the wavelength range from 300 to 600 nm. b) Photoelectrochemical transient at a wavelength of 325 nm. c) IMPS response at a wavelength of 369 nm. d) Total reflectance spectra in the wavelength range from 200 to 800 nm. e) Linear sweep voltammetry under chopped solar light in 1 M KOH. For other experiments an electrolyte of 0.1 M Na_2SO_4 was used (V vs Ag/AgCl) if not stated otherwise.

Figure 4a illustrates the comparison of photocurrent spectra plotted as incident-photon-current-efficiency (IPCE) (calculated using Equation (3)) as a function of wavelength. According to the experimental findings, DEG spaced nanotubes show the highest IPCE with 40 % at a wavelength of 325 nm. Close-packed NTs demonstrate a similar spectral shape and reach a second highest IPCE with 35 % followed by DMSO NTs with 28 %. The inset graph of Figure 4a shows the determination of an indirect band-gap of tubular arrays; accordingly, we determined the band gap of DEG NTs as 3.05 eV and of DMSO and EG NTs as 3.06 eV.

The photocurrent transients were measured at a wavelength of 325 nm and are presented in Figure 4b. According to these data, DEG based NTs give the highest photocurrent response that is followed by EG and DMSO NTs. The transients show variations among the tubular structures; for instance, in the case of DEG SP NTs, the anodic photocurrent has a spike when the light is switched on, indicating the separation of photogenerated electron-hole pairs at the semiconductor/electrolyte interface that is regarded as an indication of surface recombination

of photogenerated charges: either holes are trapped by reduced species in the electrolyte or the photogenerated electrons are transferred to the holes trapped at the surface states. After the current spike, the anodic photocurrent slowly decreases until steady-state is reached. The shape of the transient is similar for DMSO SP NTs and EG based CP NTs; such a shape can be ascribed to a trap filling mechanism. On the other hand, the photocurrent transients after switching the light-off show a slow decay with time, illustrating the relaxation of electrons injected to the conduction band.

We further evaluated the electron transport behavior for the three arrays by intensity modulated photocurrent spectroscopy (IMPS) measurements, at a wavelength of 369 nm, see Figure 4c. The transport time constant is calculated using Equation (4) that is given in the experimental section. All transport time constants decay due to a higher injected electron density at higher photon flux. According to the experimental findings, the SP NTs have about one order of magnitude lower transport time constant, showing that the charge carrier transport is faster (shortest electron transport time and a suppressed charge recombination) than a close-packed morphology. Only a minor difference in the charge transport time constants of DMSO and DEG SP NTs is observed, that can be due to better organized small tube stacks between DEG based nanotubes.

To examine the optical behavior of tubes, the total reflectance was measured in the range from 200 to 800 nm, see Figure 4d. All spaced tube morphologies display a weak reflection below an irradiation wavelength of 300 nm, and at higher wavelengths stronger reflection is observed, corresponding to the band gap of TiO_2 at around 3 eV. Note that the refractive indices of TiO_2 are reported as 2.72 for rutile and 2.52 for anatase over the wavelength range of interest.^[56] Therefore, a stronger reflection is obtained between 350 to 410 nm for the nanotubular layers, and the shift in the reflectance peak positions for the different tubular arrays is attributed to varying anatase-rutile phase compositions of tubular layers leading to shifts in interference maxima.

Overall, EG CP NTs display higher total reflectance (in the UV and visible range), which indicate a higher light scattering capability due to the “denser” TiO_2 present. The reflectance of SP NTs is lower than for CP NTs, representing the better light absorption behavior of SP NTs. This shows that spacing between nanotubes leads to interspace absorption of light in the UV and visible range. Namely, due to the spacing, light is absorbed in much deeper parts in the tubular layer (in the wavelength range of interest). This light trapping can explain the improved photoelectrochemical response when SP NTs are used as a photoelectrode. Therefore, although

in total less absorber material is present, the higher absorption can be beneficial for the photoconversion efficiency.

Figure 4e compiles the results of water splitting on EG close-packed and DEG, DMSO spaced nanotubes. The transient photocurrent is recorded under chopped solar illumination in 1 M KOH. The onset potentials of DEG, DMSO spaced and EG close-packed nanotubes, which are determined when the sample is irradiated, are similar. In general, among the three morphologies, DEG based SP NTs show the highest water splitting activity that is followed by DMSO spaced nanotubes and EG close-packed nanotubes. As an illustration, under simulated solar illumination the water oxidation photocurrent reaches 0.15 mA cm^{-2} for DEG based SP NTs at 0.8 V (vs Ag/AgCl), while EG CP NTs exhibit three times lower photocurrent, 0.05 mA cm^{-2} . It is evident that the space formation is due to the presence of an ordered small tube network in the spacing, which improves the charge transfer and the light absorption (as well as light penetration) characteristics of tubes, however, here charge transfer plays a key role in governing the photoelectrochemical behavior.

Figure 5. a) Equivalent circuit for fitting the EIS plots. Impedance spectra in a bode plot of b) EG, c) DMSO and d) DEG based nanotubes obtained at a voltage range from -0.5 V to 0.5 V with a step width of 0.2 V in 0.1 M Na₂SO₄ (V vs. Ag/AgCl), under dark.

We also carried out EIS measurements in 0.1 M Na₂SO₄ electrolyte in the voltage range from (-0.5 V) to (0.5 V) with a step width of 0.1 V under dark conditions. The measured and fitted absolute impedance and phase as a function of frequency are shown in Figure 5. The obtained resistance and CPE values (EG, DMSO and DEG NTs) as a result of fitting the profiles are given in Table S1. The acquisition of two phase constants is attributed to the compact-like barrier layer and porous nanotubular structure. This can be well presented with two RCPE

circuits connected in series and connected with the solution resistance (R_s) in series, as illustrated in Figure 5a. R_s is a solution resistance, R_{out} , CPE_{out} are the resistance and the constant phase element of the porous layer, while in higher frequency range, R_{in} and CPE_{in} show the resistance and the constant phase element of the inner barrier layer (space charge layer), see also Table S1. The solution resistances of these different morphologies are similar except for minor variations. The resistance of the outer and inner layer increases with the applied voltage. This arises from the degree of band bending as a function of the applied potential.^[57] Therefore, an increase in the charge transfer resistance of the outer porous layer as well as of the inner barrier layer with applied potential is attributed to band bending, which forms a barrier against charge carrier transfer. Conversely, the CPE capacitance (CPE_{out} and CPE_{in}) of TiO₂ NTs decays with the potential and this can be ascribed to a thicker depletion layer (space charge layer width).

The data fitted by the equivalent circuit show that the resistance of the outer layer is the highest for EG based nanotubes, followed by that of DMSO and DEG based nanotubes. This finding is in line with the varying areal tube densities. While EG based tubular layer has the highest tube density, DEG has the lowest tube density that will affect the resistance of the porous layer to electrolyte penetration and diffusion of ionic species. Accordingly, Chen et al. observed lower charge transfer resistance for close-packed nanotubes with small spacing in comparison with close-packed nanotubular arrays without spacing in EIS measurement.^[58] Conversely, SP NTs have higher CPE_{in} and CPE_{out} than a close-packed morphology and the values decay with the applied potential. The variation in CPE for the different morphologies is ascribed to the varying surface properties, such as conductivity of the oxide or the surface porosity, in line with the literature.^[57] As evident from the Bode plot, at low frequencies all structures have a phase angle of 80° that deviate slightly from a pure capacitive behavior (90°, double layer charging).

Further electrochemical impedance spectroscopy measurements were performed for close-packed and spaced nanotubular arrays under light (369 nm) to elucidate the influence of illumination on the charge transfer behavior, see Figure S7 in Supporting Information. For all tubular arrays, the impedance decreases almost one order of magnitude, which illustrates the lower charge transfer resistance than under dark conditions. This may originate from the charge carrier generation and the effective separation of electron-hole pairs under illumination and consequently the decay of the space charge layer's resistance, as typical for an n-type semiconductor under illumination. Accordingly, under illumination, the Bode phase plot exhibits a similar trend; i.e. the phase angle decreases and shifts to higher frequencies, which is

attributed to the charge carrier generation under UV light. Overall, the charge transfer resistance that indicates the charge transfer across the solid/liquid interface is clearly lower than in the case of dark conditions.

Overall, the spaced nanotubes grown in DEG show the lowest charge transfer resistance and the shortest electron transfer times in IMPS. This makes them most effective in photoelectrochemical applications such as photoelectrochemical water splitting.

Conclusions

Within this work, we investigated and compared the morphological features and resulting electrochemical as well as photoelectrochemical performance of DEG, DMSO based spaced and EG based close-packed TiO₂ nanotubular arrays. The morphological variations influence the resulting electrical, optical, electrochemical and photoelectrochemical properties of nanotubular arrays. For instance, close-packed tubes provide a higher surface area and thus may show higher electrochemical activity. However, in view of the photoelectrochemical activity, spaced nanotubular arrays photoelectrochemically outperform close-packed nanotubes. For example, spaced nanotubes exhibit two times higher photocurrent in photoelectrochemical water oxidation. This can be ascribed to a significantly better light trapping characteristics of spaced tubes and a faster charge transport behavior (i.e., one order of magnitude lower transport time than close-packed nanotubes). Additionally, an enhanced charge transfer behavior is also confirmed with electrochemical impedance measurements under dark and light conditions; i.e., the EG based close-packed nanotubes exhibit higher resistance to charge transfer than spaced nanotubes. Clearly, space initiation and the presence of an ordered small tube network in the spacing enhance the charge transfer.

We believe that these findings illustrate how controlled spacing over self-ordered nanotubes can be used to optimize their electrochemical and photoelectrochemical performance.

Experimental Section

Anodization – Thermal treatment

To grow nanotubes, 0.1 mm thick Ti foil (99.6 % pure temper annealed, ADVENT) was used. The synthesis of spaced NTs consists of a two-step anodization process. In the first step, the Ti foil was anodized in 0.5 wt% NH₄F and 2 M H₂O containing ethylene glycol (EG) at 80 V for 10 min, and then the nanotube layer was removed by ultrasonication in deionized water (DIW). In the second step, spaced TiO₂ NTs were formed in DMSO with additions of 4 wt% HF (40 % Sigma Aldrich), 7 wt% H₂O (H₂O content of HF is also considered in the calculations), and 0.3 wt% NH₄F at an anodization voltage of 30 V, and an anodization temperature of 30°C for 1 h.

In the case of DEG based spaced nanotubes, anodization was performed in an electrolyte containing DEG, 2 wt% HF (40 % Sigma Aldrich), 0.3 wt% NH₄F and 1 wt% H₂O at 30 V for 15 h at room temperature. As a reference, we used close-packed NTs that were prepared in 0.1 M NH₄F and 4 M H₂O containing EG electrolyte at 40 V, 50 °C for 15 min.

For anodization, a two-electrode configuration was used in which Pt acts as a cathode, and the Ti substrate acts as an anode (1.5 cm inter-electrode distance in 30 ml electrolyte). Afterwards, the samples were immersed in ethanol overnight and dried in a N₂ stream.

In order to crystallize the as-formed TiO₂ nanotubes, samples were annealed at 450 °C for 1 h in air with a heating/cooling rate of 30 °C min⁻¹ using a Jetfirst Rapid Thermoannealer (RTA, Jipelec, France).

Morphological characterization

The morphology of the NTs was examined by a field-emission scanning electron microscope (FE-SEM S4800 Hitachi) equipped with an energy-dispersive X-ray (EDX) analyser. In this study, all the geometrical features were measured from SEM images using the Image J software and the values are the average of at least fifteen measurements.

To analyse the crystallinity of tubular layers, X-ray diffraction (XRD, X'pert Philips MPD with a Panalytical X'celerator detector) was conducted utilizing graphite monochromized CuK α radiation (Wavelength 1.54056 Å). The mass fractions of anatase and rutile were calculated by means of Equation (1)^[59] using the anatase (101) and rutile (110) peaks:

$$X = 1/[1 + 2.265(I_R/I_A)] \quad (1)$$

where X is the mass fraction of anatase and I_A (I_R) is the diffraction peak intensity of anatase (rutile) phase.

The approximate crystallite size was determined from the peak broadening of XRD reflections by the Scherrer formula^[60] given in Equation (2):

$$D = k\lambda/(\beta \cos \theta) \quad (2)$$

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 (0.15418 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 was characterized with X-ray photoelectron spectroscopy (XPS, PHI 5600, USA). XPS measurements were performed on a high-resolution X-ray photoelectron spectrometer (PHI 5600) using monochromatic Al K α radiation (1486.6 eV, 300 W) for excitation (peaks shifted with C1s 284.8 eV). Sputter depth profiles were obtained by Ar⁺ sputtering with a sputter rate of 2.2 nm/min.

Photoelectrochemical and electrochemical characterization

The incident photon to current conversion efficiency (IPCE) was measured at a voltage of 0.5 V (vs. Ag/AgCl) in 0.1 M Na₂SO₄ recorded between 300 to 600 nm utilizing an Oriel 6365 150 W Xe-lamp equipped with an Oriel Cornerstone 7400 1/8 m monochromator. It was calculated for each wavelength according to Equation (3):

$$IPCE(\%) = (I_{ph} \times h\nu/P \times \lambda) \times 100 \quad (3)$$

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

To determine the charge carrier transport rate, intensity modulated photocurrent spectroscopy (IMPS) measurements were carried out by a Zahner IM6 (Zahner Elektrik, Kronach, Germany) with an UV modulated light ($\lambda=369$ nm) in 0.1 M Na₂SO₄ solution. The range of frequency was modulated from 1 mHz to 1 kHz. The transport time constant was estimated using Equation (4).

$$\tau_T = 1/2\pi f_T \quad (4)$$

where τ_T is a transport time constant with a unit of second (s) and f_T is a characteristic frequency minimum of the IMPS imaginary component with a unit of hertz (s⁻¹).

Linear sweep voltammetry was conducted under a simulated AM 1.5 (100 mW cm^{-2}) illumination provided by a solar simulator (300 W Xe with an optical filter, Solarligh, RT) in 1 M KOH electrolyte. Photocurrent vs. voltage characteristics was recorded by scanning the voltage from -0.8 V to + 1.0 V at a scan rate of 1 mV s^{-1} by a Jaissle IMP 88 PC potentiostat in the dark and the light.

Note that the electrochemical and the photoelectrochemical measurements were performed in a three-electrode configuration, consisting of TiO_2 nanotubes as a photoanode, platinum as a counter and Ag/AgCl (3 M KCl) as a reference electrode (if not stated otherwise).

The total reflectance was measured by an Avantes spectroscopy system with AvaLight-DH-S-BAL balanced power source and AvaSpec-2048L Starline versatile fiber-optic spectrometer detector (PTFE that was utilized as a reference standard).

In order to examine the charge transfer characteristics, electrochemical impedance spectroscopy (EIS; IM6, Zahner, Germany) measurements were performed in a three-electrode setup with Ag/AgCl (3 M KCl) as a reference, Pt as a counter and TiO_2 NTs as a working electrode in 0.1 M Na_2SO_4 . Measurements were carried out by applying amplitude of 10 mV in the frequency range from 100 kHz to 10 mHz.

Acknowledgements

The authors acknowledge the ERC, the DFG, the DFG “Engineering of Advanced Materials” cluster of excellence and DFG “funCOS”. The authors also thank to Helga Hildebrand for X-ray photoelectron spectroscopy and Ulrike Marten-Jahns for X-ray diffraction analyses.

Keywords: charge transfer • nanotubes • photocurrent • spaced TiO_2 nanotubes • water splitting

- [1] M. Assefpour-Dezfuly, C. Vlachos, E. H. Andrews, *J. Mater. Sci.* **1984**, *19*, 3626-3639.
- [2] V. Zwillling, E. Darque-Ceretti, A. Boutry-Forveille, D. David, M. Y. Perrin, M. Aucouturier, *Surf. Interface Anal.* **1999**, *27*, 629-637.
- [3] D. Gong, C. A. Grimes, O. K. Varghese, W. Hu, R. S. Singh, Z. Chen, E. C. Dickey, *J. Mater. Res.* **2001**, *16*, 3331-3334.
- [4] R. Beranek, H. Hildebrand, P. Schmuki, *Electrochem. Solid-State Lett.* **2003**, *6*, B12-

B14.

- [5] K. Lee, A. Mazare, P. Schmuki, *Chem. Rev.* **2014**, *114*, 9385-9454.
- [6] P. Roy, S. Berger, P. Schmuki, *Angew. Chem., Int. Ed.* **2011**, *50*, 2904-2939.
- [7] D. Kim, A. Ghicov, S. P. Albu, P. Schmuki, *J. Am. Chem. Soc.* **2008**, *130*, 16454-16455.
- [8] C. Das, P. Roy, M. Yang, H. Jha, P. Schmuki, *Nanoscale* **2011**, *3*, 3094-3096.
- [9] F. Riboni, N. T. Nguyen, S. So, P. Schmuki, *Nanoscale Horiz.* **2016**, *1*, 445-466.
- [10] I. Hwang, S. So, M. Mokhtar, A. Alshehri, S. A. Al-Thabaiti, A. Mazare, P. Schmuki, *Chem. - A Eur. J.* **2015**, *21*, 9204-9208.
- [11] C. Ruan, M. Paulose, O. K. Varghese, G. K. Mor, C. A. Grimes, *J Phys. Chem. B* **2005**, *109*, 15754-15759.
- [12] S. P. Albu, P. Schmuki, *Phys. Status Solidi RRL* **2010**, *4*, 215-217.
- [13] S. Yoriya, G. K. Mor, S. Sharma, C. A. Grimes, *J. Mater. Chem.* **2008**, *18*, 3332-3336.
- [14] S. Yoriya, *Int. J. Electrochem. Sci.* **2012**, *7*, 9454-9464.
- [15] Y. Chen, H. Lu, X. Wang, S. Lu, *J. Mater. Chem.* **2012**, *22*, 5921-5923.
- [16] N. K. Allam, C. A. Grimes, *Langmuir* **2009**, *25*, 7234-7240.
- [17] M. Uchida, S. Chiba, R. Tomiha, M. Masaki, N. Shirai, *Electrochemistry* **2002**, *70*, 418-420.
- [18] W.-Y. Rho, H.-S. Kim, W.-J. Chung, J. S. Suh, B.-H. Jun, Y.-B. Hahn, *Appl. Surf. Sci.* **2018**, *429*, 23-28.
- [19] M. Wang, D. Guo, H. Li, *J. Solid State Chem.* **2005**, *178*, 1996-2000.
- [20] K. Ketpang, K. Lee, S. Shanmugam, *ACS Appl. Mater. Interfaces* **2014**, *6*, 16734-16744.
- [21] G. F. Ortiz, I. Hanzu, T. Djenizian, P. Lavela, J. L. Tirado, P. Knauth, L. Tirado, *Chem. Mater.* **2009**, *21*, 63-67.
- [22] G. D. Salián, B. M. Koo, C. Lefevre, T. Cottineau, C. Lebouin, A. T. Tesfaye, P. Knauth, V. Keller, T. Djenizian, *Adv. Mater. Technol.* **2018**, *3*, 1700274.
- [23] J. M. Macak, M. Zlamal, J. Krysa, P. Schmuki, *Small* **2007**, *3*, 300-304.

- [24] J. F. de Brito, F. Tavella, C. Genovese, C. Ampelli, M. V. B. Zanoni, G. Centi, S. Perathoner, *Appl. Catal., B* **2018**, *224*, 136-145.
- [25] L. Zhao, H. Wang, K. Huo, L. Cui, W. Zhang, H. Ni, Y. Zhang, Z. Wu, P. K. Chu, *Biomaterials* **2011**, *32*, 5706-5716.
- [26] Y. Zhu, Q. Wang, L. Zhang, W. Zhao, J. Xu, H. Chen, *ChemElectroChem* **2017**, *4*, 1011-1015.
- [27] M.-H. Seo, M. Yuasa, T. Kida, J.-S. Huh, K. Shimano, N. Yamazoe, *Sens. Actuators, B* **2009**, *137*, 513-520.
- [28] N. Liu, H. Mirabolghasemi, K. Lee, S. P. Albu, A. Tighineanu, M. Altomare, P. Schmuki, *Faraday Discuss.* **2013**, *164*, 107-116.
- [29] R. P. Lynch, A. Ghicov, P. Schmuki, *J. Electrochem. Soc.* **2010**, *157*, G76-G84.
- [30] G. Liu, N. Hoivik, K. Wang, *Electrochem. Commun.* **2013**, *28*, 107-110.
- [31] P. E. de Jongh, D. Vanmaekelbergh, *Phys. Rev. Lett.* **1996**, *77*, 3427-3430.
- [32] K. Zhu, T. B. Vinzant, N. R. Neale, A. J. Frank, *Nano Lett.* **2007**, *7*, 3739-3746.
- [33] F. Cao, G. Oskam, G. J. Meyer, P. C. Searson, *J. Phys. Chem.* **1996**, *100*, 17021-17027.
- [34] S. Ozkan, A. Mazare, P. Schmuki, *Electrochim. Acta* **2015**, *176*, 819-826.
- [35] K. Zhu, N. R. Neale, A. F. Halverson, J. Y. Kim, A. J. Frank, *J. Phys. Chem. C* **2010**, *114*, 13433-13441.
- [36] X. Chen, S. S. Mao, *Chem. Rev.* **2007**, *107*, 2891-2959.
- [37] K. Ozawa, M. Emori, S. Yamamoto, R. Yukawa, S. Yamamoto, R. Hobara, K. Fujikawa, H. Sakama, I. Matsuda, *J. Phys. Chem. Lett.* **2014**, *5*, 1953-1957.
- [38] M. Hattori, K. Noda, T. Nishi, K. Kobayashi, H. Yamada, K. Matsushige, *Appl. Phys. Lett.* **2013**, *102*, 43105.
- [39] G. W. An, M. A. Mahadik, W.-S. Chae, H. G. Kim, M. Cho, J. S. Jang, *Appl. Surf. Sci.* **2018**, *440*, 688-699.
- [40] S. Ozkan, A. Mazare, P. Schmuki, *Electrochim. Acta* **2018**, *268*, 435-447.
- [41] S. Ozkan, N. T. Nguyen, A. Mazare, R. Hahn, I. Cerri, P. Schmuki, *Electrochem.*

- Commun.* **2017**, 77, 98-102.
- [42] S. Ozkan, N. T. Nguyen, I. Hwang, A. Mazare, P. Schmuki, *Small* **2017**, 13, 1603821.
 - [43] S. Ozkan, G. Cha, A. Mazare, P. Schmuki, *Nanotechnology* **2018**, 29, 195402.
 - [44] S. P. Albu, A. Ghicov, S. Aldabergenova, P. Drechsel, D. LeClere, G. E. Thompson, J. M. Macak, P. Schmuki, *Adv. Mater.* **2008**, 20, 4135-4139.
 - [45] N. Liu, K. Lee, P. Schmuki, *Angew. Chem., Int. Ed.* **2013**, 52, 12381-12384.
 - [46] J.-H. Xing, Z.-B. Xia, J.-F. Hu, Y.-H. Zhang, L. Zhong, *J. Electrochem. Soc.* **2013**, 160, C239-C246.
 - [47] M. Nischk, P. Mazierski, Z. Wei, K. Siuzdak, N. A. Kouame, E. Kowalska, H. Remita, A. Zaleska-Medynska, *Appl. Surf. Sci.* **2016**, 387, 89-102.
 - [48] H. Habazaki, K. Fushimi, K. Shimizu, P. Skeldon, G. E. Thompson, *Electrochem. Commun.* **2007**, 9, 1222-1227.
 - [49] V. Vega, J. M. Montero-Moreno, J. García, V. M. Prida, W. Rahimi, M. Waleczek, C. Bae, R. Zierold, K. Nielsch, *Electrochim. Acta* **2016**, 203, 51-58.
 - [50] H. Park, W. Choi, *J. Phys. Chem. B* **2004**, 108, 4086-4093.
 - [51] A. M. Czoska, S. Livraghi, M. Chiesa, E. Giamello, S. Agnoli, G. Granozzi, E. Finazzi, C. Di Valentin, G. Pacchioni, *J. Phys. Chem. C* **2008**, 112, 8951-8956.
 - [52] O. K. Varghese, D. Gong, M. Paulose, C. A. Grimes, E. C. Dickey, *J. Mater. Res.* **2003**, 18, 156-165.
 - [53] D. Fang, Z. Luo, K. Huang, D. C. Lagoudas, *Appl. Surf. Sci.* **2011**, 257, 6451-6461.
 - [54] S. P. Albu, H. Tsuchiya, S. Fujimoto, P. Schmuki, *Eur. J. Inorg. Chem.* **2010**, 2010, 4351-4356.
 - [55] S. Bauer, A. Pittrof, H. Tsuchiya, P. Schmuki, *Electrochem. Commun.* **2011**, 13, 538-541.
 - [56] T. Kijima, *Inorganic and Metallic Nanotubular Materials: Recent Technologies and Applications*, Springer Berlin, **2010**.
 - [57] M. E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy*, **2008**.

- [58] B. Chen, J. Hou, K. Lu, *Langmuir* **2013**, 29, 5911-5919.
- [59] R. A. Spurr, H. Myers, *Anal. Chem.* **1957**, 29, 760-762.
- [60] A. L. Patterson, *Phys. Rev.* **1939**, 56, 978-982.

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Optimized spacing between TiO₂ nanotubes for enhanced light harvesting and charge transfer

A regular spacing between TiO₂ nanotubes leads to a better light trapping characteristics and a faster charge transfer behaviour.