Suppressing Deep Traps in Self-Organized TiO₂ Nanotubes by Nb Doping and Optimized Water Content

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This manuscript reports on the photoelectrochemical properties of anodized 0.1 and 0.15 at% Nb-doped NTs prepared using electrolytes containing different amount of water (2 to 12 wt%). It is shown that Nb-doped NTs perform better than undoped NTs, achieving a photocurrent density up to 1.35 mA/cm² at 1 V vs RHE when the water content is sufficiently high (12 wt%). The IPCE also confirms the superiority of Nb-doped NTs, again the larger values (55% IPCE at 300 nm) are obtained when using 12 wt% H₂O in the electrolyte. EIS analysis and capacitance measurements highlight the peculiarity of the Nb-doped TiO₂ NTs which behave differently than undoped NTs. The electron transport resistance in Nb-doped NTs is similar (10³ Ω cm²) to the one of undoped NTs. However, Nb-doped NTs exhibit larger electron mobility and require lower activation energy for electron transport (i.e. a less negative bias) than undoped NTs. Furthermore, Nb-doping, combined with an optimal water content of 12 wt%, is found to be an effective strategy to fully suppress the formation of deep intra band-gap energy states. The presence of Nb in the TiO₂ lattice dictates the fate and the energy of defects introduced during anodization and annealing. These defects are shallower than those observed in undoped NTs.

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Anodized TiO₂ nanotubes (NTs)¹ exhibit very appealing photoelectrochemical properties, enriched by the possibility of 1D charge transport, orthogonal charge separation at the nanoscale^{2,3} and by the presence of long-lived electrons.⁴ Consequently, they have received great attention over the last 15 years, with research efforts aimed at (i) understanding the growth mechanism behind the formation of the NTs^{1,5,6} and (ii) optimizing their performances in dye-sensitized solar cells (DSSCs),⁷ solar water splitting⁸ photocatalysis⁹ as well as biomedicine¹⁰ and sensing.¹¹ Remarkable progress has been made on the synthesis of the NTs and, as a result, the anodizing parameters can now be finely tuned to grow NTs up to 100–1000 μm long^{1,5} or advanced anodic morphologies (i.e. highly ordered arrays, bamboo or multilayers NTs).² Titanium dioxide is by far the most important photocatalyst¹² and the majority of the research on anodized TiO₂ NTs have been devoted to the study of their photochemical properties. The current perception is that the photochemistry of the NTs is dictated by the geometry (i.e. length, diameter, wall thickness, smooth vs rough NTs)⁹ and by the crystallinity (i.e. anatase vs rutile).^{13,14} Less attention has instead been given to the influence of defects on the photoelectrochemical and electron transport properties of the NTs. Defects can be introduced during the anodizing step (also by adding foreigner species in the electrolyte), during the heat-treatment step necessary to crystallize the NTs and by ion implantation.¹⁵ For example the Schmuki's group have reported on the effect of N doping (achieved by annealing in an ammonia environment) on the photoactivity of the NTs,¹⁶ again observing that the photoresponse of the NTs is strongly dependent on the length of the NTs film. It is also likely that a certain amount of oxygen vacancies can be induced in the NTs upon annealing due to the significant present of C species (coming from the organic electrolyte used during the anodization) in as-prepared NTs.^{17,18} Park et al.¹⁹ have demonstrated that a carbon thermal treatment triggers a visible photo-response in the NTs. Some recent contributions^{20–27} have partly shed light on the correlation between defects and photoactivity. It is found that the wall thickness has no significant influence on the charge-carrier lifetimes and that fast-trapping immobilizes carrier on time scales of a few tens of picoseconds (one order of magnitude faster than in nanoparticles), suggesting there is a much higher density of trap states in TiO₂ NTs.²⁰ It is very important to identify optimal anodizing conditions to reduce the concentration of trap states to improve charge transport within the NTs.²⁴ The density of deep traps within the NTs can be partially reduced by increasing the water content in the anodizing electrolyte.^{21–23} The anodizing potential is

also a key factor in determining the photoactivity of the NTs;^{25–27} a study conducted at potential ranging from 15 to 60 V revealed that at 30 V the anodizing process is more reproducible and the NTs films are more photoactive.²⁷ An anodizing potential of (or close to) 30 V may be optimal for electron transport;²⁷ some researchers believe that such optimal potential promotes a preferential growth of the anatase crystals in the (004) plane; these crystals pile up creating a fiber-like structure with enhanced transport properties along the NTs in the [001] direction, perpendicular to the plane of the Ti substrate.²⁸ Interestingly, the same preferential orientation can also be obtained using low water contents (2 wt%) electrolytes.²⁹ Despite efforts to understand the impact of defects on photoactivity and to minimize (i.e. optimize) their presence in the TiO₂ anodic films to reduce recombination, TiO₂ NTs are found to be still highly defective,³⁰ rich in deep intra-bandgap states³¹ and electron mobility in NTs is as low as in nanoparticles despite their 1D ordered morphology.^{32–34} Deep traps can be passivated by electrochemical doping,³⁵ however it is paramount to found alternative strategies to prevent their formation and progress toward optimal photochemical properties.

In an attempt to increase the conductivity of the NTs and improve the collection of electrons, a mild doping (0.1–0.2 at.%) with Nb (i.e. anodizing Ti-Nb alloys) has proven to be a very efficient strategy to enhance the photoelectrochemical properties of TiO₂ NTs.^{36–38} Nb-doping of the NTs has also been achieved by using a fluoroniobate complex in the anodizing bath.³⁹ Furthermore, Nb-doped NTs have great potential in photocatalysis,⁴⁰ DSSCs⁴¹ and as transparent conductive electrodes.^{42,43}

The explanation of why a mild Nb doping is so beneficial to photochemistry and electron transport remains somewhat vague. For example, it is not clear why the conductivity of Nb doped TiO₂ NTs should decrease by increasing the Nb content from none to 0.2 at.% when the NTs are annealed at 450°C, as reported by Ref. 37; these authors suggest that Nb doping can only be activated by annealing the NTs at 650°C. The reason for the need of such activation is again rather unclear. To summarize, the understanding of why Nb-doping is beneficial to the photoelectrochemistry of the NTs deserve further attention.

Aim of the work.—The aim of this work is to investigate in depth the combined impact of Nb-doping and water content in the electrolyte on the formation of defects and on the photoelectrochemical properties of TiO₂ NTs. Defects associated with excess electrons introduced by Nb-doping are expected to be shallow (i.e. close to the bottom of the conduction band of TiO₂).⁴⁴ However, additional defects are introduced during the anodization process (depending on the oxygen

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available for the growth of the oxide) and during annealing of the NTs (as-prepared NTs are rich in carbon contaminations¹⁷ and some of the oxygen of TiO₂ is stripped away from the oxide during the thermal treatment). Therefore the role of doping on tailoring the defect properties is not simple to understand. Electrochemical impedance spectroscopy is used to investigate whether the presence of Nb has any influence on the nature and energy of the defects. Whereas in undoped NTs we found that a large portion of these defects are still associated with deep traps,²³ the energy states of the entire amount of defects is shallower in Nb-doped NTs. Our results show unequivocally that the Nb-doped NTs behave very differently than the undoped NTs. Nb doping, when aided by a sufficiently high (12 wt%) water content in the anodizing electrolyte, is a very effective approach for suppressing the formation of deep trap energy states in the NTs. Hence, the presence of Nb in the TiO₂ lattice has also an impact on the formation, density and energy of the defects which are induced in the NTs during the anodization²⁷ and during the annealing.⁴⁵

Experimental

Anodization.—Prior to anodizing, the Ti and Ti-Nb alloy (0.1 and 0.15 at.% Nb) specimens (grade II, Hauner Metallische Werkstoffe, HMW, Germany) were mechanically grinded with SiC sand paper (Buehler-Mett II, P320 and P1000) and ultrasonically cleaned in isopropyl alcohol, then rinsed with distilled water and ethanol using a Vibra-cell sonicator (20 kHz, power output 70 W). Anodization was carried out using a Keithley 2450 source-meter and a two electrodes cell (Ti and Ti-Nb anode and a Pt cathode) at 30 V, using an ethylene glycol, EG, (Sigma Aldrich) containing 0.1 M NH₄F (Sigma Aldrich) and an amount of water varying from 2 wt% to 12 wt%. Anodization time was varied from a minimum of 20 min to a maximum of 60 min. It has been recently shown that for water contents of 2 to 3.5 wt% in EG containing 0.1 M NH₄F, the best photoelectrochemical properties are achieved in undoped NTs grown for 20 min and approximately 1.1 μ m long, whereas longer anodizing times leads to longer NTs (up to 2.3 μ m after 60 min) with lower photoelectrochemical response.⁴⁶ Therefore in this study the maximum anodizing time for undoped and Nb-doped NTs grown in 2 wt% H₂O has been kept to 20 min. Anodizing times for undoped NTs and Nb-doped NTs grown in 12 wt% H₂O has been instead varied from 20 to 60 min, considering that the growth of the NTs is slower when the EG electrolyte contains an increased amount of water. This has allowed to compare the photochemical behavior of undoped and Nb-doped NTs grown in 2 wt% and 12 wt% H₂O, all having similar length. In an attempt to find the optimal length/photoelectrochemical response of undoped TiO₂ NTs (which are cheaper than Nb-doped TiO₂ NTs, since they are grown out of grade II Titanium, 99.6% pure) we have also investigated anodizing time larger than 60 min. However we have found out that 60 min. is the optimal anodizing time and when extending the process longer we observe a decrease in the photoelectrical response. Results are summarized in Table S1, in supportive information.

As-prepared anodized samples were rinsed with water, ultrasonically cleaned with ethanol and finally converted to anatase by thermal heat-treatment at 450°C^{17,47} in air (heating rate: 100°C/h, dwelling time: 1 h, furnace type: LHT 04/17, Nabertherm).

Morphology, Microstructure & Crystallinity. The morphology and the microstructure of the photoelectrodes were analyzed by Scanning Electron Microscopy (SEM) using a Field Emission Nova NanoSEM 230 (Nova FEI). SEM has also been used to estimate the length, wall thickness and diameter of the NTs (measuring at least 10 different NTs). Crystallinity of the annealed specimens was investigated by X-Ray Diffraction (Bragg-Brentano mode, θ - 2θ), using a Panalytical, X'Pert Pro instrument (Cu-K α 1, λ = 1.5406 Å).

Photoelectrochemical measurements.—The photocurrent density measurements were performed using a Voltalab80 PGZ-402 (Radiometer Analytical) potentiostat. A three electrodes set-up (TiO₂ NTs Working Electrode, a Pt plate/XM120, Radiometer Analytical

Counter Electrode and a Ag/AgCl/3 M-KCl/XR300, Radiometer Analytical Reference Electrode) was fitted in a Cappuccino Cell⁴⁸ filled with 1 M KOH. A Potential sweep from -900 to +700 mV (scan rate of 20 mV/sec) was applied between the working and the reference electrodes. For the photocurrent density (J_{photo}) measurements, the TiO₂ NTs photoanode was irradiated by a Xe lamp (solar simulator, L.O.T-Oriel AG), at an intensity of 80 mW/cm². Incident Photon to Current Efficiency (IPCE) analysis was performed using a Xe lamp (L.O.T-Oriel AG) and a monochromator (Omni- λ 300, L.O.T-Oriel AG). The TiO₂ NTs photoanodes were immersed in 1 M KOH and irradiated at different wavelengths (λ) ranging from 550 to 300 nm, while applying a potential bias of 0.23 V (Keithley 2450) vs the counter electrode.

Electrochemical impedance spectroscopy (EIS).—EIS was performed by using a Voltalab80 PGZ-402 (Radiometer Analytical) potentiostat, a Cappuccino Cell⁴⁸ filled with 1 M KOH and a three electrodes set up. Measurements were carried out in the dark at potentials from +250 mV to -1000 mV vs Ag/AgCl (50 mV interval). For each potential the frequency was swept from 100 KHz to 100 mHz with modulation amplitude of 10 mV.

Results and Discussion

For brevity, the discussion of the anodizing curves, the electrolyte conductivity, the XRD and SEM analysis is limited to undoped TiO₂ NTs. The same results and conclusions also apply to 0.1 and 0.15 at.% Nb doped TiO₂ NTs.

The current density vs time transients for anodization conducted at 30 V in EG containing 0.1 M NH₄F and amount of H₂O varying from 2 to 12 wt%, are reported in Fig. 1. Such water contents are sufficient for the formation of the NTs, whereas in electrolytes with lower water content nanopores are formed.^{49,50} All the curves in Fig. 1 show the typical shape expected for the formation of TiO₂ NTs,⁵ that is an initial decrease of the current density down to a minimum before porosity becomes significant and the current density begins to increase before reaching a steady state. The amount of water in the electrolyte influences the value of the current density. The minimum current density value of each curve, achieved within the first 100 sec of the anodization process, decreases when going from 2 to 3.5, 6 and 8 wt% H₂O, whereas it increases in 12 wt% H₂O media. Additional information are provided by the conductivity measurement conducted on the different electrolyte and summarized in Fig. 2; the conductivity increases as a function of the water content, being around 625 μ S/cm at 2 wt% H₂O and over 1000 μ S/cm at 12 wt% H₂O. This is in line with a previous report from Acevedo-Peña et al.⁵¹ and it is expected

Figure 1. Current density vs time transient recorded during anodization of Ti in EG containing 0.1 M NH₄F, as a function of H₂O content (2–12 wt%).

Figure 2. Conductivity of the EG electrolytes, containing also 0.1 M NH_4F , as a function of H_2O content (2–12 wt%).

since water has higher conductivity than EG (additionally there is preferential dissolution of NH_4F in water, rather than EG, once sufficient water is available and this is also beneficial to the conductivity of the electrolyte). As the water content is increased, the chemical dissolution of the anodized TiO_2 film by the action of fluoride ions in the electrolyte becomes also more significant. This can partly explain why for a given anodizing time, as discussed later in the manuscript, NTs are shorter whenever grown in an electrolyte with an increased amount of H_2O .

The XRD analysis of undoped TiO_2 NTs grown in electrolytes with different water content is summarized in Fig. 3. Similar XRD spectra were also observed for Nb-doped NTs, see supporting information, Fig. S1 and Fig. S2. As expected, following annealing at 450°C ,¹⁷ only anatase peaks are detected. Amongst TiO_2 polymorphs, anatase is the most performing in photoelectrochemical applications due to its higher electron mobility⁵² and lower charge carriers recombination rate.³ The water content does not seem to influence significantly the crystalline phase, however for very low water content (2 wt%), an additional peak at $2\theta = 27^\circ$ can be detected in the XRD spectrum; it is likely due to some sub-stoichiometric TiO_{2-x} oxide, indicating that the H_2O content is too low to sustain optimal growth of TiO_2

Figure 3. XRD spectra of undoped TiO_2 NTs grown using different water content in the anodizing electrolyte.

Table I. Ratio between the intensities of (101) and (004) anatase XRD peaks of undoped and Nb-doped TiO_2 NTs, as a function of water content in the anodizing electrolyte.

Water Content	(101)/(004) XRD peak intensity ratio in TiO_2 NTs		
	Undoped NTs	0.1 at.% Nb doped NTs	0.15 at.% Nb doped NTs
2 wt% H_2O	0.5	0.4	0.4
3.5 wt% H_2O	0.8	0.3	0.5
8 wt% H_2O	1.5	2.8	3.0
12 wt% H_2O	1.5	3.0	2.7

during anodization. By comparing the anatase peaks at 25.3° and 38° corresponding to the (101) and (004) plane respectively, it is possible to evaluate whether there is a preferential crystallographic orientation in the NTs. In the case of non-preferential growth (i.e. no texture), the most intense peak is that at 25.3° corresponding to the (101) plane. The ratio between the intensities of (101) and (004) anatase peaks as a function of the water content are given in Table I. In agreement with the literature,^{28,29} for low water content (2 and 3.5 wt%) we observe preferential growth along the (004) plane as the peak at 38° is the most intense (i.e. the ratio (001)/(004) is <1). The preferential orientation along the (004) plane is instead less significant for 8 and 12 wt% water content, where the most intense peak belongs to the (101) plane. Exactly the same trend is observed in undoped and Nb-doped NTs (Fig. S1 and Fig. S2 in supporting information), as summarized in Table I. Interestingly, the intensity ratio (101)/(004) for water contents of 8 and 12 wt% is 1.5 for undoped NTs, whereas it is close to 3.0 in Nb-doped NTs, see Table I. This suggests that in Nb-doped NTs, providing the water content is sufficiently high (8–12 wt%), the formation of (101) crystals is more pronounced than in undoped NTs. Previous reports^{28,29} suggest that the piling up of (004) anatase crystals leads to a fiber-like structure in the [001] direction, normal to the plane of the Ti substrate) and facilitate electron transport in the NTs. However, on the basis of our previous findings, a low water content is detrimental to the photoelectrochemistry of the NTs, as the oxygen deficiency in the electrolyte translates into a higher density of defects.²³ The beneficial effect of high (12 wt%) water content on the photochemistry of NTs due to the growth of less defective NTs (when oxygen is abundant in the electrolyte) is indeed confirmed in this work, as discussed below. Hence regarding the preferential growth along the (004) plane our conclusions are different from those reported in literature.^{28,29} We suggest that whenever the oxygen content is below a critical threshold (i.e. below 3.5 wt% H_2O), the NTs are more defective and these defects, particularly deep traps, are better accommodated into the (004) anatase crystals, hence there is a preferential growth in the [001] direction. From Table I, it also clear that the presence of Nb in the TiO_2 lattice, combined with an optimal water content (8–12 wt%) facilitates the formations of (101) rather than (004) anatase crystals. A more in depth investigation, such as TEM-EELS (beyond the scope of this work, ongoing and to be reported elsewhere), is required to unveil the link between (004) crystals and the presence of deep traps in the NTs.

Microstructure of the oxide.—The water content in the electrolyte has an impact on the microstructure and the morphology of the NTs. As it can be appreciated from the SEM images in Figs. 4a–4b, showing the top view and the cross section of NTs grown 20 min. at 30 V in electrolytes containing 2 wt% and 12 wt% H_2O , the water content also affects the final length of the NTs. The length of the NTs shortens from 1.3 μm to $0.8\div0.9\ \mu\text{m}$ as the water content increases from 2 wt% to 12 wt%. In order to obtain a similar length to NTs grown in 2 wt% H_2O , NTs formed at 12 wt% H_2O have to be anodized at 30 V for 60 min., Fig. 4c. Additionally, the remnant of the barrier layer formed during the early stages of the anodization is covering the top of the NTs grown for 20 min. (see Figs. 4a–4b) whereas it becomes less significant (i.e. it has almost been completely dissolved) after

Figure 4. Top view and cross section of TiO_2 NTs grown for 20 min. at 30 V in EG containing 0.1 M NH_4F and 2 wt% H_2O (a) or 12 wt% H_2O (b). NTs grown for 60 min. at 30 V in 12 wt% H_2O are instead shown in (c).

60 min. (Fig. 4c). An anodizing time of 20 min. was chosen as a starting point of this work, as we recently observed that it allowed optimal photoelectrochemical response in NTs grown in low water content (2 to 3.5 wt%) electrolytes.⁴⁶ One may argue that such short time is not sufficient to completely remove the remnant part of the porous layer that covers the top of the NTs, as clearly shown in Figs. 4a–4b. It is true that the top-porous layer and the nanograss (another additional contribution to disordered NTs, due to chemical dissolution of the top of the NTs leading to partial collapse and clumping/clustering of the NTs when anodizing time is extended above 60 min.) negatively affect the performance of the NTs in photocatalysis⁵³ and dye sensitized solar cells (DSSCs)⁵⁴ because the 1D transport across the NTs is lost and recombination triggered. In DSSCs the dye loading is also

negatively affected. It is important to highlight that Albu et al.⁵⁵ have also developed a nice strategy to eliminate the presence of the top porous layer and nanograss.

Nevertheless, we expect that the porous layer covering the top of the NTs, visible in Figs. 4a–4b, to have not a significant influence on the photochemistry of the NTs, regarding the solar water splitting process. It does not seem to prevent penetration of the electrolyte within the NTs and it is only few nm thick. Furthermore, according to Eagles,⁵⁶ the light penetration depth is approximately 10 nm at $\lambda = 300$ nm and 1 μm at $\lambda = 380$ nm. If anything the top porous layer may have a minor effect only at very short λ , close to 300 nm.

A summary of the effect of H_2O content on the NTs length is given in Fig. 5a; as already mentioned above the longest NTs are grown at 2 wt% H_2O and the shortest NTs are grown at 12 wt% H_2O . The type of substrate (undoped vs Nb doped) has no influence on the final length of the NTs, which is instead determined by applied potential (30 V), the water (2 to 12 wt%) and the fluoride (0.1 M) contents. The anodizing bath becomes more aggressive as the water content is increased, hence more of the anodic oxide is dissolved and the length of the NTs is shorter. On the contrary, the donation of oxygen to Ti is more difficult at 2 wt% water content and therefore there is a reduced tendency to form the anodic oxide film. As a result, low water content leads to the formation of a thinner barrier layers (at the metal/oxide interface, i.e. at the bottom of the NTs) during the early stages of anodization.⁵⁷ Ionic transport throughout this thinner layer is therefore facilitated and this also explains the larger growing rate observed when using 2 wt% water.⁵⁸

The amount of water in the electrolyte has also an influence on the inner and outer diameter of the NTs, both becoming larger as the water content is increased, Figs. 5b–5c. The relationship between the water content and the inner and outer diameter is almost linear and, again, it is not affected by the type of substrate (undoped vs doped) used for the anodization. The wall thickness of the NTs (measured at the NTs top) does not change significantly in function on the water content, Fig. 5d. However, as a trend, slightly smaller values of wall thickness (approximately 14 to 16 nm) are observed at low water content (2 wt%) and slightly larger values (between 16 and 22 nm) at high water content (12 wt%).

Photoelectrochemical properties of undoped and doped TiO_2 NTs.—Fig. 6 shows the photocurrent density (at 1 V vs RHE) of undoped and Nb-doped TiO_2 NTs as a function of the water content. In good agreement with the literature^{27,36,37} the results show that Nb-doped specimens exhibit better photoelectrochemical properties than undoped TiO_2 . There is no much difference in terms of performances between 0.1 at.% and 0.15 at.% Nb-doped TiO_2 . This results were obtained on NTs annealed at 450°C and photocurrent density values (and IPCE discussed later) are in line with those reported by Schmuki's group;^{36,37} therefore our results put into question the necessity to activate the Nb doping at 650°C, as instead inferred by these authors.^{36,37}

As a general trend, Fig. 6, the photochemical response of the undoped TiO_2 is enhanced by increasing the amount of water in the electrolyte. For example, the photocurrent density of undoped TiO_2 is approximately 0.75 mA/cm^2 for 2 wt% H_2O content and increases to 0.95 mA/cm^2 for 12 wt% H_2O . The higher photo-response has been very recently ascribed to the lower density of intra band-gap deep energy states (located at 0.35 and 0.55 eV below the conduction band) in TiO_2 NTs grown in high water content electrolytes.^{21–23} For a fixed anodizing potential of 30 V, the density of deep traps in undoped TiO_2 NTs has been estimated to be $6 \cdot 10^{18} \text{ cm}^{-3}$ and $2 \cdot 10^{18} \text{ cm}^{-3}$ for 2 wt% and 12 wt% H_2O respectively.²³ In the case of Nb-doped TiO_2 NTs the values of photocurrent are similar (from 0.9 to 1.1 mA/cm^2) for water content between 2 wt% and 12 wt%. However, as previously discussed the length of the NTs shortens as the water content increases. For a meaningful comparison it is therefore necessary to consider NTs of similar length to those grown at 2 wt% H_2O . Similar length of NTs could be achieved by increasing the anodizing time from 20 min to

Figure 5. Effect of H₂O content in the electrolyte on length (a), inner diameter (b), outer diameter (c) and wall thickness (d) of TiO₂ NTs.

60 min. when working at 12 wt% H₂O. It is clear that for both undoped and 15 at.% Nb-doped NTs anodized for 60 min., the photo-response increases to 1.1 mA/cm² and 1.35 mA/cm², respectively. From Fig. 6,

Figure 6. Effect of H₂O content in the electrolyte and of the type of substrate (undoped and Nb doped) on the photocurrent density of TiO₂ NTs.

it can therefore be concluded that Nb-doped TiO₂ has larger photoactivity than undoped TiO₂ and that a higher H₂O content is beneficial to both undoped and doped TiO₂, particularly when comparing NTs of similar length.

Electron collection and transport properties of the NTs have been investigated by IPCE analysis. Figs. 7a–7b reports the results by IPCE of undoped and Nb-doped TiO₂ NTs grown at 2 and 12 wt% H₂O content for 20 min. As expected IPCE of Nb-doped TiO₂ NTs is larger than for undoped ones. The IPCE value also increase by increasing the water content (2 vs 12 wt%). This confirms that electron transport within the NTs is aided by the Nb-doping and by the amount of water in the electrolyte. Extending the anodizing time to 60 min. for a water content of 12 wt%, in order to achieve a comparable length to NTs grown using 2 wt% H₂O, there is still a further improvement in the IPCE response. Fig. 7c shows an increase of the IPCE value up to 43% for undoped NTs and 55% for Nb-doped NTs at 300 nm. Taking into account the light penetration depth in TiO₂,⁵⁶ electrons generated from photons of $\lambda = 300$ nm have to travel across the entire NTs film before being collected at the Ti electrode. The very good IPCE of 55% for Nb-doped NTs is a clear indication of their higher electron mobility.

Additionally, the higher IPCE values in the region 300–330 nm of the NTs photoelectrodes grown in 12 wt% H₂O, Figs. 7b and 7c may also due to the fact that the top of those NTs is almost completely from the irregular top porous layer, see Figs. 4b–4c which is the remnant of the barrier layer formed during the early stages of the anodization.

Figure 7. Effect of the water content in the electrolyte, 2 wt% (a) and 12 wt% (b) and of the type of substrate (undoped vs Nb doped) on the IPCE response of TiO_2 NTs anodized for 20 min. The IPCE response is increased for both undoped and Nb-doped TiO_2 NTs by anodizing for 60 min. (c).

How can the higher photoactivity of Nb-doped TiO_2 NTs toward solar water splitting be interpreted? The improved photoresponse of Nb-doped TiO_2 can be explained in terms of a valence induction effect leading to the formation of Nb^{5+} and Ti^{3+} in regular lattice sites in the bulk of anatase TiO_2 .^{44,59} That is, the excess electrons introduced by Nb doping are released into the anatase lattice, producing Ti^{3+} centers that shift the Fermi level to a position very close to the conduction band of TiO_2 . However, it is important to understand also the nature of additional defects introduced into the doped system during the anodization and the post-growth annealing. As-prepared NTs are amorphous and rich in carbon contaminations¹⁷ as they are grown

in organic electrolytes. Thermal annealing is therefore required to crystallize the NTs and decompose the organic remnants. Due to the presence of carbon and the fact the NTs are mostly annealed in air, further defects (oxygen vacancies for example) are formed during the thermal treatment. Defect states in TiO_2 are of fundamental importance in several applications, including photocatalysis. The nature of these states, often referred to as “ Ti^{3+} centers”, is rather complex and at least four different kinds of Ti^{3+} ions are known to exist in anatase TiO_2 ,⁶⁰ with energies between 0.1 to 0.8 eV below the conduction band (E_{CB}) bottom.³⁴ In a recent EIS study we have identified shallow traps states 0.1 eV below E_{CB} and deep traps states at 0.3 eV and 0.6 eV below E_{CB} in undoped TiO_2 NTs.²³ Such analysis is still missing for Nb-doped TiO_2 NTs and it is addressed here. Studies on nanoparticles suggest that charge carrier recombination occurs at deep trap sites associated with surface states and defects such as oxygen vacancies.⁴⁵ A similar scenario can be foreseen for the TiO_2 NTs. Shallowly trapped charge carriers can transfer to deep traps, from which thermal escape is then not possible²⁰ and recombination occurs. In anatase nanowires, nanoparticles and NTs deep traps have been linked to grain boundaries, hence surface states.⁶¹

Pioneer contributions to the study of the EIS behavior of the NTs were published by Muñoz and co-workers.^{62,63} The NTs were described as being composed of a duplex structure with an (i) oxide at the bottom of the pores/tubes and (ii) a NTs wall with different donor density and surface state concentrations.^{62,63} Similar conclusions have been recently put forward also by Miraghaei et al.;⁶⁴ in particular these researchers also propose a model where the capacitance of the TiO_2 NTs is affected by their geometry. At anodic potential (with respect to the E_{FB}) the capacitance is mainly determined by the bottom of the NTs and the barrier layer underneath the NTs (i.e. NTs wall is not active), whereas at more cathodic potentials regions the wall of the NTs becomes active as electrons are injected from the substrate (metallic Ti) to the conduction band of TiO_2 . As a result at cathodic potentials (again with respect to the E_{FB}), the NTs behave like a porous metallic electrode and high capacitance values are observed (due also to the NTs large surface area).⁶⁴ Supercapacitance at cathodic potential have also been reported by Fabregat-Santiago and co-workers.⁶⁵

As our EIS analysis of undoped NTs is reported elsewhere,²³ here we focus on the doped NTs, particularly the 0.15 at.% Nb-doped system, Figs. 8a–8b. The model used to fit the EIS data is also given in Figs. 8a–8b and allows to estimate the transport resistance, (R_{Tr}) at the bottom of the NTs (including a contribution from the barrier layer formed underneath the NTs upon annealing at 450°C) and the resistance to charge transfer (R_{CT}) at the oxide/electrolyte interface. From Fig. 8a it emerges that the Nb-doped system grown at 2 and 12 wt% H_2O content exhibit a similar R_{Tr} , approximately $10^3 \Omega \text{ cm}^2$ at anodic (positive) potentials. However, as the system move toward more cathodic (negative) potentials, the behavior of the NTs is different. The R_{Tr} of the NTs grown at 12 wt% H_2O drops to approximately $10 \Omega \text{ cm}^2$ at -350 mV vs Ag/AgCl whereas for NTs grown at 2 wt% water content R_{Tr} drops to $10 \Omega \text{ cm}^2$ at -650 mV vs Ag/AgCl. This is an indication that for 12 wt% H_2O content there is a lower activation energy for electron transport. In conclusion the electron mobility at the bottom of NTs grown at 12 wt% H_2O is larger than at 2 wt% H_2O content. The values of R_{Tr} are comparable to those reported for undoped systems.²³ The NTs are highly defective^{30,31} and it is known that electron transport within the NTs is rate limiting.⁶⁶ Considering the mild doping (0.1 and 0.15 at.% Nb), it is likely that electron transport is still limiting the performance of the NTs. Nevertheless Fig. 8a, suggests that the electron mobility (μ_e) is larger in Nb-doped NTs as electron transport is activated at a less cathodic potential. A precise measurement of the electron mobility (μ_e) would required resistivity measurements on a single NTs,⁴² however it can be assumed that R_{Tr} reflects the resistivity of the bottom of the NTs. As μ_e is given by $1/(N_d \cdot e \cdot \rho)$ where e is the elementary charge, N_d the defects density and ρ the resistivity, it can be inferred that being R_{Tr} similar for both undoped and doped NTs, μ_e is larger and therefore N_d is lower in Nb-doped NTs. The resistance to charge transfer, R_{CT} , Fig. 8b, is also slightly lower at 12 wt% H_2O content in comparison with 2 wt% H_2O

Figure 8. Transport resistance (a) and Charge Transfer resistance (b) of Nb-doped TiO_2 NTs grown using 2 wt% and 12 wt% H_2O content.

and again decreases at a less negative potential for high water content. From Fig. 8b it is possible to gain further information on the Nb-doped TiO_2 NTs. It is known that a dip in the charge transfer resistance corresponds to the filling of intra band-gap energy states.⁶⁷ In Nb-doped NTs grown at 2 wt% H_2O content there are dips at -400 mV vs Ag/AgCl and -650 mV vs Ag/AgCl. As the conduction band, E_{CB} , is located between -750 and -800 mV vs Ag/AgCl (estimation based on the photocurrent onset potential,⁶⁸ see supplementary information Figs. S3a-b), those dips correspond to deep traps situated at 0.35 eV below E_{CB} and shallow states 0.1 eV below E_{CB} . In Nb-doped NTs grown using 12 wt% H_2O there is only a dip at -650 mV vs Ag/AgCl which is ascribed to shallow states 0.1 eV below E_{CB} . Hence Fig. 8b suggests that deep traps are totally suppressed in Nb-doped TiO_2 NTs when using 12 wt% H_2O .

To gain a further understanding on the nature of the intra band-gap states the capacitance response of the Nb-doped TiO_2 NTs at low frequency (1 Hz and 100 mHz) was investigated. The presence of deep electronic states within the fundamental band-gap can only be investigated at a sufficiently low frequency (≤ 1 Hz).^{62,63,69} The results are reported in Figs. 9a–9b and in Table II, where the density and the location of the energy states is given also for the undoped NTs previously studied.²³ In non-ideal semiconductors, due to the presence of defects, instead of a band-gap there is a mobility gap formed with states at lower energies than the bandgap.⁷⁰ Zang et al.³¹ estimate that up to $5 \cdot 10^4$ electrons can be stored in deep traps state within a single NTs at sufficiently negative (cathodic) bias. TiO_2 nanostructures are characterized by an exponential tail of surface shallow states located below E_{CB} and deep traps located 0.5 eV below E_{CB} and associated

Figure 9. Volumetric capacitance of Nb-doped NTs grown in 2 wt% (a) and 12 wt% H_2O (b), measured at low frequency (1 Hz–100 mHz).

with incomplete coordinated Ti surface sites.⁷¹ NTs submitted to a strong negative bias at a basic pH exhibit an increase in conductivity and capacitance (leading to supercapacitance if bias is hold for an extended time at strongly negative values).^{64,65} A peak in the capacitance is an indication of an energy state being filled with electrons. From Figs. 9a–9b, the remarkable electronic structure of Nb-doped TiO_2 can be appreciated. There is no evidence of the presence of deep trap states located at 0.5 to 0.6 eV below the conduction band since no peak is observed at -200 mV vs Ag/AgCl. These deep states were instead previously observed in undoped NTs,^{21–23} limiting their photochemical properties. It is clear that Nb-doped TiO_2 NTs present

Table II. Density of deep and shallow traps estimated from capacitance measurements at a frequency of 100 mHz for undoped and Nb-doped NTs grown at different water content.

Water content	Undoped TiO_2 NTs ²³		0.15 at.% Nb doped NTs	
	2 wt.%	12 wt.%	2 wt.%	12 wt.%
Deep traps density (10^{18} cm^{-3})	6	2	1	-
Shallow traps density (10^{18} cm^{-3})	2	2	4	3
Deep + Shallow traps density (10^{18} cm^{-3})	8	4	5	3

very different electronic structure in comparison with undoped NTs. The effect of the water on the density of the intra-bandgap states is also very clear in Figs. 9a–9b. Whereas in the 2 wt% H₂O NTs there is still a shoulder peak at –450 mV vs Ag/AgCl, which can be ascribed to a residual density of deep traps located at 0.3 eV below E_{CB} , such peak is absent in the NTs grown using 12 wt% H₂O. Both systems present a shoulder peak at –650 mV vs Ag/AgCl which is due to shallow donor states at 0.1 eV below E_{CB} . The majority of intra-bandgap states in Nb-doped NTs grown in 12 wt% H₂O are therefore located very close (if not within) the E_{CB} edge. Due to the suppression of deep traps, the defect density (N_d), calculated using the approach proposed by Oskam et al.⁷² adapted to TiO₂ NTs,²² is lower and shallower in Nb-doped NTs than in undoped NTs, Table II. The ability of Nb-doped NTs, especially when supported by sufficiently high water content, to accommodate all the defects at shallow energy states is truly remarkable. Our EIS analysis, combined with the XRD results previously discussed, see Table I, strongly suggests that deep traps are located preferentially in (004) anatase crystals, as these crystallographic plane is particularly abundant in NTs grown at 2 wt% H₂O and can be minimized by combining an optimum water content (12 wt%) with Nb doping. Interestingly, a recent contribution⁴⁴ on Nb-doped TiO₂ nanoparticles studied by EPR spectroscopy also highlights the ability of the Nb-doped system to accommodate additional defects (introduced by reduction) as shallow donor levels corresponding to Ti³⁺ sites situated into the bulk of the lattice rather than at the surface.⁴⁴ Our work (with evidences from XRD, IPCE and EIS) reveals therefore strong similarities in the behavior of TiO₂ NTs and nanoparticles and although an EPR analysis has not been conducted within this work, we suggest that the shallow energy states we observe in Nb-doped NTs are indeed to be associated with Ti³⁺ centers in the bulk of the anatase lattice. On the contrary, the deep energy states that were previously identified in the undoped NTs can be ascribed to surface defects,^{61,70,71} which are very likely associated with (004) anatase crystals. The study here presented, was limited to Nb-doped NTs grown for a maximum time of 60 min; it would be interesting to find out in future work whether by extending the anodizing time above 60 min. the photoelectrochemical properties of the Nb-doped NTs can be further enhanced. This will be addressed in a future publication. Nevertheless, since Ti-Nb alloy are rather expensive in comparison with grade II Titanium (99.6%), it is also useful to understand how the photochemistry of undoped TiO₂ NTs can be improved. We have indeed conducted studies on undoped TiO₂ NTs anodized for time longer than 60 min (90 to 120 min) in EG containing 12 wt% H₂O (previous study showed already that for 2 to 3.5 wt% H₂O content the optimal anodizing time is 20 min.⁴⁶) to verify whether we could further enhance the photocurrent density of such arrays. Nevertheless, we have observed that the optimum anodizing time for undoped NTs grown in EG with 12 wt% H₂O content is of 60 min. Above 60 min., the NTs start to collapse and form clusters and the photocurrent density decreases. A summary of the results can be found in Table S1 (supportive information).

Conclusions

From the photoelectrochemical analysis of the Nb-doped TiO₂ NTs grown by using different water content (2 to 12 wt% H₂O) it emerges that deep traps states can be completely suppressed by combining the Nb doping with an optimal (12 wt%) water content. This combination leads to the formation of NTs with higher electron collection efficiency as clearly shown by the photocurrent density, IPCE and EIS measurements. It can therefore be concluded that the Nb-doped system behaves differently from the undoped NTs, as further confirmed by the XRD analysis. It appears as the presence of Nb in the TiO₂ lattice not only scatters the excess electrons on Ti³⁺ centers located in the bulk of the anatase lattice, but also dictates the fate of additional defects which are introduced in the NTs during the anodizing and the annealing steps. In undoped NTs deep traps, likely to be associated with (004) anatase crystals, cannot be fully suppressed; however in Nb-doped NTs defects are shallower and beneficial to the

photochemical properties of the NTs. The IPCE (maximum 55% in Nb-doped NTs) and the EIS analysis show that there is still work to do to achieve 100% electron collection efficiency. The NTs are still too defective and electron transport is too slow. A possible approach to lower the resistance to electron transport of the NTs could be the use of a water content higher than 12 wt% in order to further reduce the number of defects, coupled with longer annealing time in oxygen to suppress formation of oxygen vacancies and allow the crystal to grow further and form larger domains. These issues will be addressed in a future work as we expect to move close to 100% IPCE efficiency. TiO₂ is by far the most important photocatalyst and the optimization of electron transport in TiO₂ NTs is needed to exploit the full potential of these fascinating 1D arrays.

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References

1. D. Regonini, C. R. Bowen, A. Jaroenworarluck, and R. Stevens, *Mater. Sci. Eng.: R. Reports*, **74**, 377 (2013).
2. K. Lee, A. Mazare, and P. Schmuki, *Chem. Rev.*, **114**(19), 9385 (2014).
3. M. Kapilashrami, Y. Zhang, Y.-S. Liu, A. Hagfeldt, and J. Guo, *Chem. Rev.*, **114**(9), 9662 (2014).
4. A. Kahnt, C. Oelsner, F. Werner, D. M. Guldi, S. P. Albu, R. Kirchgeorg, K. Lee, and P. Schmuki, *Appl. Phys. Lett.*, **102**(23), 233109 (2013).
5. P. Roy, S. Berger, and P. Schmuki, *Angew. Chem. Int. Ed. Engl.*, **50**(13), 2904 (2011).
6. X. Zhou, N. T. Nguyen, S. Özkan, and P. Schmuki, *Electrochim. Comm.*, **46**, 157 (2014).
7. P. Roy, D. Kim, K. Lee, E. Spiecker, and P. Schmuki, *Nanoscale*, **2**(1), 45 (2010).
8. A. Fujishima and K. Honda, *Nature*, **238**(5358), 37 (1972).
9. I. Paramasivam, H. Jha, N. Liu, and P. Schmuki, *Small*, **8**(20), 3073 (2012).
10. K. Huo, B. Gao, J. Fu, L. Zhao, and P. K. Chu, *RSC Adv.*, **4**(33), 17300 (2014).
11. V. Galstyan, E. Comini, G. Faglia, and G. Sberveglieri, *Sensors*, **13**(11), 14813 (2013).
12. A. Fujishima, X. Zhang, and D. Tryk, *Surf. Sci. Reports*, **63**(12), 515 (2008).
13. N. Liu, I. Paramasivam, M. Yang, and P. Schmuki, *J. Solid State Electrochem.*, **16**(11), 3499 (2012).
14. J. Liu, P. M. Hosseinpour, S. Luo, D. Heiman, L. Menon, D. A. Arena, and L. H. Lewis, *J. Vacuum Sci. & Tech. A*, **33**(2), 021202 (2015).
15. A. Ghicov, J. M. Macak, H. Tsuchiya, J. Kunze, V. Haeublein, L. Frey, and P. Schmuki, *Nano Letters*, **6**(5), 1080 (2006).
16. J. M. Macak, A. Ghicov, R. Hahn, H. Tsuchiya, and P. Schmuki, *J. Mater. Res.*, **21**(11), 2824 (2006).
17. D. Regonini, A. Jaroenworarluck, R. Stevens, and C. R. Bowen, *Surf. Interf. Analysis*, **42**(3), 139 (2010).
18. D. Regonini, A. Satka, A. Jaroenworarluck, D. W. E. Allsopp, C. R. Bowen, and R. Stevens, *Electrochim. Acta*, **74**, 244 (2012).
19. J. H. Park, S. Kim, and A. J. Bard, *Nano Letters*, **6**(1), 24 (2005).
20. C. Wehrenfennig, C. M. Palumbiny, H. J. Snaith, M. B. Johnston, L. Schmidt-Mende, and L. M. Herz, *J. Phys. Chem. C*, **119**(17), 9159 (2015).
21. L.-k. Tsui, T. Homma, and G. Zangari, *J. Phys. Chem. C*, **117**(14), 6979 (2013).
22. L.-k. Tsui and G. Zangari, *Electrochim. Acta*, **121**(0), 203 (2014).
23. D. Regonini, A. Groff, G. D. Sorarù, and F. J. Clemens, *Electrochim. Acta*, **186**, 101 (2015).
24. A. Mohammadpour, P. Kar, B. D. Wiltshire, A. M. Askar, and K. Shankar, *Curr. Nanosci.*, **11**(5), 593 (2015).
25. P. Acevedo-Pena and I. Gonzalez, *J. Electrochem. Soc.*, **160**(8), H452 (2013).
26. S. P. Albu and P. Schmuki, *Electrochim. Acta*, **91**, 90 (2013).
27. D. Regonini, A. Schmidt, C. G. Aneziris, T. Graule, and F. J. Clemens, *Electrochim. Acta*, **169**, 210 (2015).
28. P. Acevedo-Pena, F. Gonzalez, G. Gonzalez, and I. Gonzalez, *Phys. Chem. Chem. Phys.*, **16**(47), 26213 (2014).
29. S. Lee, I. J. Park, D. H. Kim, W. M. Seong, D. W. Kim, G. S. Han, J. Y. Kim, H. S. Jung, and K. S. Hong, *Energy & Environ. Sci.*, **5**(7), 7989 (2012).
30. R. Beranek, H. Tsuchiya, T. Sugishima, J. M. Macak, L. Taveira, S. Fujimoto, H. Kisch, and P. Schmuki, *Appl. Phys. Lett.*, **87**(24), 243114 (2005).

31. Q. Zhang, V. Celorrio, K. Bradley, F. Eisner, D. Cherns, W. Yan, and D. J. Fermín, *J. Phys. Chem. C*, **118**(31), 18207 (2014).
32. J. R. Jennings, A. Ghicov, L. M. Peter, P. Schmuki, and A. B. Walker, *J. Am. Chem. Soc.*, **130**(40), 13364 (2008).
33. C. Richter and C. A. Schmittenmaer, *Nat. Nano.*, **5**(11), 769 (2010).
34. Z. Guo, O. V. Prezhdo, T. Hou, X. Chen, S.-T. Lee, and Y. Li, *J. Phys. Chem. Lett.*, **5**(10), 1642 (2014).
35. L.-k. Tsui, M. Saito, T. Homma, and G. Zangari, *J. Mater. Chem. A*, **3**(1), 360 (2015).
36. C. Das, P. Roy, M. Yang, H. Jha, and P. Schmuki, *Nanoscale*, **3**(8), 3094 (2011).
37. M. Yang, H. Jha, N. Liu, and P. Schmuki, *J. Mater. Chem.*, **21**(39), 15205 (2011).
38. L. Pei, M. Yang, D. Zhang, L. Zhang, P. Chen, Y. Song, and Y. Gan, *RSC Adv.*, **5**(12), 9138 (2015).
39. T. Cottineau, N. Bealu, P.-A. Gross, S. N. Pronkin, N. Keller, E. R. Savinova, and V. Keller, *J. Mater. Chem. A*, **1**(6), 2151 (2013).
40. M. Wang, J. Iocozia, L. Sun, C. Lin, and Z. Lin, *Energy & Environ. Sci.*, **7**(7), 2182 (2014).
41. M. Yang, D. Kim, H. Jha, K. Lee, J. Paul, and P. Schmuki, *Chem. Comm.*, **47**(7), 2032 (2011).
42. Y. Alivov, V. Singh, Y. Ding, L. J. Cerkovnik, and P. Nagpal, *Nanoscale*, **6**(18), 10839 (2014).
43. A. Yahya, S. Vivek, D. Yuchen, and N. Prashant, *Nanotech.*, **25**(38), 385202 (2014).
44. J. Biedrzycki, S. Livraghi, E. Giamello, S. Agnoli, and G. Granozzi, *J. Phys. Chem. C*, **118**(16), 8462 (2014).
45. U. Diebold, *Surf. Sci. Reports*, **48**(5–8), 53 (2003).
46. D. Regonini and F. J. Clemens, *Mater. Lett.*, **142**, 97 (2015).
47. A. Jaroenworarluck, D. Regonini, C. R. Bowen, and R. Stevens, *Appl. Surf. Sci.*, **256**(9), 2672 (2010).
48. R. Van de Krol and M. Gratzel, *Photoelectrochemical Hydrogen Production*, Springer, New York (2012).
49. W. Wei, S. Berger, C. Hauser, K. Meyer, M. Yang, and P. Schmuki, *Electrochem. Comm.*, **12**, 1184 (2010).
50. W. Wei, S. Berger, N. Shrestha, and P. Schmuki, *J. Electrochem. Soc.*, **157**(12), C409 (2010).
51. P. Acevedo-Peña, L. Lartundo-Rojas, and I. González, *J. Solid State Electrochem.*, **17**(11), 2939 (2013).
52. H. Tang, K. Prasad, R. Sanjinès, P. E. Schmid, and F. Lévy, *J. Appl. Phys.*, **75**(4), 2042 (1994).
53. A. Mazzarolo, K. Lee, A. Vicenzo, and P. Schmuki, *Electrochem. Comm.*, **22**, 162 (2012).
54. K. Zhu, T. B. Vinzant, N. R. Neale, and A. J. Frank, *Nano Letters*, **7**(12), 3739 (2007).
55. S. P. Albu and P. Schmuki, *Phys. Status Solidi (RRL) – Rapid Res. Lett.*, **4**(7), 151 (2010).
56. D. M. Eagles, *J. Phys. Chem. Solids*, **25**(11), 1243 (1964).
57. A. Valota, D. J. LeClere, P. Skeldon, M. Curioni, T. Hashimoto, S. Berger, J. Kunze, P. Schmuki, and G. E. Thompson, *Electrochim. Acta*, **54**(18), 4321 (2009).
58. S. A. Ali Yahia, L. Hamadou, A. Kadri, N. Benbrahim, and E. M. M. Sutter, *J. Electrochem. Soc.*, **159**(4), K83 (2012).
59. S. Livraghi, M. Chiesa, M. C. Paganini, and E. Giamello, *J. Phys. Chem. C*, **115**(51), 25413 (2011).
60. C. Di Valentin, G. Pacchioni, and A. Selloni, *J. Phys. Chem. C*, **113**(48), 20543 (2009).
61. M. Jankulovska, T. Berger, S. S. Wong, R. Gómez, and T. Lana-Villarreal, *ChemPhysChem*, **13**(12), 3008 (2012).
62. A. G. Muñoz, Q. Chen, and P. Schmuki, *J. Solid State Electrochem.*, **11**(8), 1077 (2007).
63. A. G. Muñoz, *Electrochim. Acta*, **52**(12), 4167 (2007).
64. S. Miraghaei, F. Ashrafizadeh, M. Santamaria, and F. Di Quarto, *Curr. Nanosci.*, **11**, 299 (2015).
65. F. Fabregat-Santiago, E. M. Barea, J. Bisquert, G. K. Mor, K. Shankar, and C. A. Grimes, *J. Am. Chem. Soc.*, **130**(34), 11312 (2008).
66. M. Stiller, J. Barzola-Quiquia, I. Lorite, P. Esquinazi, R. Kirchgeorg, S. P. Albu, and P. Schmuki, *Appl. Phys. Lett.*, **103**(17), 173108 (2013).
67. S. Gimenez, H. K. Dunn, P. Rodenas, F. Fabregat-Santiago, S. G. Miralles, E. M. Barea, R. Trevisan, A. Guerrero, and J. Bisquert, *J. Electroanal. Chem.*, **668**, 119 (2012).
68. R. Beranek, *Adv. Phys. Chem.*, **2011**, 1 (2011).
69. L. V. Taveira, A. A. Sagüés, J. M. Macak, and P. Schmuki, *J. Electrochem. Soc.*, **155**(6), C293 (2008).
70. T. Berger, D. Monllor-Satoca, M. Jankulovska, T. Lana-Villarreal, and R. Gómez, *ChemPhysChem*, **13**(12), 2824 (2012).
71. J. Bisquert, F. Fabregat-Santiago, I. Mora-Seró, G. García-Belmonte, E. M. Barea, and E. Palomares, *Inorg. Chim. Acta*, **361**(3), 684 (2008).
72. G. Oskam, S. J. C., P. M. Hoffmann, and P. C. Searson, *J. Electrochem. Soc.*, **143**, 2531 (1996).