Preparation and Characterization of TiO₂ Nanotube Arrays in Ionic Liquid for Water Splitting

R.G. Freitas, M.A. Santanna, E.C. Pereira

NANOFUEL – LIEC – Departamento de Química. Universidade Federal de São Carlos – C.P.: 676 – CEP: 13565-905, São Carlos, SP, Brazil

1. Introduction

Efficient splitting of water into H₂/O₂, photocatalytically activated, is probably the most desired pathway to convert abundant solar energy into “hydrogen”, the proposed clean energy carrier of the future. The total amount of solar energy impinging on the earth’s surface in one year is about 3x10²⁴ J, or approximately 10⁴ times the worldwide yearly consumption of energy [1]. The search for efficient conversion of solar energy into other useful forms is, in view of the increasing anxiety over the exhaustion of fossil energy resources and attendant global warming, one of the most important challenges for future.

However, there are three major important tasks for the solar production of hydrogen: (1) Stability. Metal oxides are the most photochemically stable semiconductors in aqueous solution, but their band-gaps are either too large (≈3.0 eV) to absorb a significant fraction of incident solar energy, or their semiconductor characteristics (e.g. charge transport) are poor [2]. (2) Band-gap values. Considering the water splitting energy of 1.23 eV and overpotential losses, the semiconductor(s) should have a band-gap greater than 1.7 eV. However, semiconductors with relative low band-gaps have been found to lack stability during water splitting [2]. (3) Energy level edge position. Even though a semiconductor may generate sufficient energy to drive an electrochemical reaction, the band edge position may prevent it from react leading to water splitting [2]. For spontaneous water splitting, water oxidation and reduction potential must lie between the valence and conduction band edges.

Among inorganic oxides, TiO₂ is an important candidate for efficiently water splitting reaction. Several papers in the literature [3,4] have demonstrated that besides the microstructure, the morphology is important to optimize the oxide properties. Then, TiO₂ nanotubes (TiO₂NT) seem to be a promise material as photoanode to water splitting application, once these nanostructures provide unique electronic properties, such as high electron mobility [5], appropriated band edge positions [6], quantum confinement effects [7], high specific surface area [8], high mechanical strength [9] and photocorrosion resistance [10]. In this scenario, TiO₂NTs seem to be a versatile compound and one of the most investigated nanostructure in materials science.

Among the factors that affect the TiO₂NT properties, electrochemically obtained, the non-aqueous electrolyte can be regarded as a very important variable. In this context, ionic liquid (IL) have many applications, such as powerful solvents and electrically conducting fluids (electrolytes). Specifically during titanium anodization, the use of a fluor salt which is liquid at ambient temperature, such as 1-butyl-3-methylimidazoliumtetrafluoroborate (BMIM-BF₄), is important as fluoride precursors source which determine the quality, morphology and density of the nanotubes. The use of liquid as electrolyte during the TiO₂NTs obtained by electrochemical means is quite recent, and just few papers have reported it. Schmuki et al. [11] observed the formation of well-ordered self-organized TiO₂ nanotube layers in BMIN-BF₄...
Table 1
Experimental conditions in which TiO$_2$NT arrays were obtained.

<table>
<thead>
<tr>
<th>TiO$_2$NT</th>
<th>Vol. % IL</th>
<th>T$^\circ$ C</th>
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<tr>
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ionic liquid electrolyte. According to the authors, by changing the potential and anodization time, the maximum thickness achieved was approximately 650 nm and the maximum diameter obtained was around 43 nm. Misra et al. [12] for the first time in the literature, synthesized double-wall vertically oriented TiO$_2$NT arrays by a simple sonochemical anodization process using BMIM-BF$_4$ ionic liquid at room-temperature. The concentric nanotubes with external diameters of around 82 and 206 nm were obtained by this process. In addition to the double-wall nature of these nanotubes, the external diameter of $>$200 nm is the largest among all the anodization processes. Teixeira et al. [13] observed that a maximum nanotube growth rate was obtained at 1.0 vol % BMIM-BF$_4$. Furthermore, the TiO$_2$ nanotubes obtained showed photocatalytic activities for the degradation of pollutants using methyl orange dye as a prototype and hydrogen generation by water splitting.

In light of this, the present study aims to investigate how structural (crystallite size) and electronic parameters (flatband potential, carrier density, width depletion layer, Debye screening length) affect the photoelectrocatalysis towards the water splitting reaction.

2. Experimental

2.1. Preparation of the TiO$_2$ nanotube arrays

Self-ordered TiO$_2$NT arrays were prepared by anodizing 1 cm$^2$ of titanium foil (99.8% Alfa Aesar) in electrolytes composed of ethylene glycol (Synth), Milli-Q water (10 vol.%) and 1-butyl-3-methyl-imidazolium-tetrafluoroborate (BMIM-BF$_4$, Sigma Aldrich) (1 or 5 vol.%). Prior to each anodization, Ti samples were ultrasonicated in acetone followed by distilled water rinses and dried in N$_2$ stream. Anodization was performed at 10 and 20$^\circ$C using a standard two-electrode cell with Ti foil as anode and a platinum foil (4 cm$^2$) as cathode, which underwent a constant applied voltage of 80 V, using a Keithley 2410 sourcemeter. The voltage was swept from the OCP to different values at $\nu = 0.1$ V s$^{-1}$, holding at the final potential value for 4 hours. The TiO$_2$NT photoelectrodes herein prepared and discussed along the text are specified in Table 1. After the anodization process, the samples were rinsed with distilled water and thermally treated at 450 $^\circ$C for 120 minutes to eliminate water, organic portions, improve its mechanical stability and to obtain the TiO$_2$-anatase crystalline phase. Soon after, a cooling rate of 5 $^\circ$C min$^{-1}$ was used.

2.2. Material Characterization

The TiO$_2$NTs morphological characterization was carried out using a Supra 35 Zeiss Field Emission Scanning Electron Microscope. The optical absorption spectra were obtained using a UV-vis spectrometer (UV-vis DRS; Cary 5G). The X-ray diffraction (XRD) patterns were obtained using a Siemens diffractometer model D5000 with CuK$_\alpha$ radiation and $\lambda = 1.5406$ Å.

2.3. Photoelectrochemical Activity and Water Splitting Generation

Photoelectrochemical measurements were performed in the photocell with a quartz ($d = 3$ cm) window. The photoelectrochemical measurements were performed using an Autolab PGSTAT-30 Potentiostat/Galvanostat. Platinum wire and TiO$_2$NTs were respectively used as counter and working electrodes. All potential were referred to the reversible hydrogen electrode (RHE). Photoelectrochemical test were carried out using 0.5M H$_2$SO$_4$ solution as electrolyte. A solar simulator (Newport Oriel Arc lamp housing 67005, Oriel xenon lamp 6285, Oriel arc lamp power supply 69907 USA) was used as light source.

3. Results and discussion

Current-time conditions obtained during the formation of the TiO$_2$ nanotube arrays films in BMIM-BF$_4$ ionic liquid at 80 V are shown in Fig. 1.

Similar current-time profiles were observed for all TiO$_2$NT electrodes. A sharp drop in current was observed in the first stage due to the formation of a barrier oxide layer; followed by an increase in current caused by the oxide layer pitting by fluoride ions and finally, the current reaches a steady value. This behaviour follows in agreement with the literature [14]. Electrodes TiO$_2$NT-1 and 2 exhibited lower current values compared to TiO$_2$NT-3 and 4, what can be related to the lower temperature (10 $^\circ$C) used during the anodization process. Additionally, it is possible to observe that the current values increase for higher ionic liquid concentrations, e.g. 1 and 5%, as can be observed for TiO$_2$NT-1, 3 (1 vol. % IL) and TiO$_2$NT-2, 4 (5 vol. % IL). Again, it agrees with the reported characteristics of Ti in $\text{F}^-$ containing electrolyte described by in the literature [15].

The surface morphology of TiO$_2$NT was investigated by FESEM microscopy and is depicted in Fig. 2.

The average pore diameter obtained at 10 $^\circ$C was around 77.5 ± 2.4 nm and 64.0 ± 2.5 nm for samples obtained in 1vol.% and 5vol.% of IL, respectively. For nanotubes obtained at 20 $^\circ$C, the pore diameter were approximately 75.8 ± 2.8 nm and 68.0 ± 2.0 nm for samples obtained in 1vol.% and 5vol.% IL, respectively. It is possible to observe that TiO$_2$NTs prepared at higher percentages of IL lead to a decreasing in the tube diameter comparing the samples prepared at the same anodization temperature. Although the TiO$_2$NT photoelectrodes do not show any significant difference from a morphologic point of view, the synthesis conditions resulted in significant differences regarding the structural and electronic properties, as will be discussed below.

![Fig. 1](https://example.com/fig1.png)
Fig. 2. FESEM images of TiO2NT arrays grown in different conditions. Tube diameter: a) TiO2NT-1, d=77.5 ± 2.4 nm, b) TiO2NT-2, d=64.0 ± 2.5 nm, c) TiO2NT-3, d=75.8 ± 2.8 nm and d) TiO2NT-4, d=68.0 ± 2.0 nm.

As can be observed by the X-ray diffraction patterns in Fig. 3, all TiO2NT samples crystallized in the anatase phase, which is characterized by peaks at 2θ = 25.281 (101) and 2θ = 48.049 (200) (JCPDS – 21-1272). The TiO2NT self-ordered film was thin, as metallic titanium peaks were also observed (JCPDS 44-1294) at higher intensities than anatase-TiO2 ones. Also, a small amount of rutile-TiO2 crystalline phase was detected at 2θ = 27.446 (110) and 2θ = 36.085 (101) (JCPDS – 21-1276).

The crystallite sizes (CS) were calculated using the Debye-Scherrer equation from the anatase (101) peak. The values obtained were 27.0, 28.0, 30.0 and 33.5 nm for TiO2NT-1, 2, 3 and 4 photoelectrode respectively, as shown in Table 2. Considering the experimental error, the CS are the same for all the prepared samples. These values are similar to those previously reported in the literature [14,16] for TiO2NT electrodes.

The band-gap, $E_g$, was estimated using the Tauc-Wood equation [17]:

$$ (a\nu)^{s} = h\nu - E_g $$

where $a$ is the absorption coefficient, $h\nu$ and $E_g$ are photon energy and optical band-gap energy, respectively. The value used for $s$ was 0.5 once TiO2 is classified an indirect gap semiconductor. $E_g$ values were thus determined by extrapolation of the linear portion of the absorption edge.

![Table 2](image)

<table>
<thead>
<tr>
<th>TiO2NT</th>
<th>C.S./nm</th>
<th>$E_B$/V</th>
<th>$N_A$/cm$^{-3}$</th>
<th>$w$/nm</th>
<th>$\lambda_0$/nm</th>
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<tr>
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<td>1.5x10$^{19}$</td>
<td>4.5</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>33.5</td>
<td>1.25</td>
<td>1.3x10$^{19}$</td>
<td>4.2</td>
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</tr>
</tbody>
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Fig. 3. XRD patterns of the TiO2NTs arrays annealed at 450°C for 2 hours. A, R, Ti represent anatase, rutile and titanium diffraction peaks respectively. a) TiO2NT-1, b) TiO2NT-2, c) TiO2NT-3 and d) TiO2NT-4.
(\textit{ahv})² curve versus the photon energy, \textit{hv}, to \( (\textit{ahv})^2 = 0 \). Concerning the TiO₂ electronic properties of, the relevant energy levels that form the band edges, and thus, define the band–gap, are considered to be the Ti3d states and O2p levels. The lowest empty energy levels are Ti4d and thus they are representative of the conduction band (CB) edge, whereas full O2p states (in particular, nonbonding \( p\pi \) states) define the valence band (VB). Both anatase and rutile show this general distribution of states [18,19]. Besides, the linear dependence of \( (\textit{ahv})^{0.5} \) on \textit{hv} indicates that TiO₂ is essentially, indirect-transition-type semiconductor. The straight-line portion of the curve, when extrapolated to zero, gives the optical band-gap \( E_g \) of 3.1–3.2 eV for all TiO₂NTs-photoelectrodes, as shown in Fig. 4. The reported band-gap values of anatase phase (bulk) is 3.2 eV [20], in agreement with the anatase-TiO₂ phase observed in Fig. 3.

TiO₂ has an indirect optical band–gap for anatase (3.2 eV) and for rutile (3.0 eV). Amorphous material is reported to have a mobility gap of about 3.2–3.5 eV [18,19]. Crucial for the optical and electrical properties, is the presence of defects that provide additional states in the band–gap near the CB or VB. Particularly important to TiO₂ are oxygen vacancies and Ti3⁺ states, which, to a large extent, dominate optical and electrical properties of the material. Typically Ti3⁺ states are situated about 0.2–0.8 eV below the conduction band [21]. Electrons may be trapped in the Ti3⁺ sites or holes may be trapped in oxygen states, leading to radicals covalently bonded to the TiO₂ surface. Such shallow defects can easily release trapped charge carries to the nearby of the conduction or valence band by thermal excitation.

Systematic photoelectrochemical measurements were carried out on the TiO₂NTs photoelectrodes. Chronoamperograms were performed to examine the photoresponse over time along light on/off cycles, as shown in Fig. 5a.

The pattern of TiO₂NTs photocurrent obtained is highly reproducible for the on/off light cycles presented, Fig. 5a. Besides, the chronoamperograms profiles, Fig. 5b, are similar to those described in the literature [22–24] for water splitting on TiO₂NTs photoelectrodes. This behaviour is attributed to the photogeneration and recombination of electron-hole pairs under on/off light conditions. Under illumination, the photoinduced electrons transport from the TiO₂NT walls to the Ti substrate rapidly to produce photocurrent. Under dark conditions, the holes recombine with electrons from the TiO₂ conduction band leading to the decrease of photocurrent.

The spike-like shape of photocurrent transients observed in Fig. 5b is a typical fingerprint of intense surface recombination process [25,26]. After the initial rise of photocurrent upon switching-on the light, a rapid decay is observed followed by a cathodic current “overshoot” after the light is switching-off. It
suggests that the photogenerated holes are being trapped in the surface states too deeply to induce efficient water oxidation and therefore, accumulating at the surface. This increases the probability of conduction band electrons to be captured, inducing recombination rather than photocurrents. When the light is interrupted, the holes accumulated in surface states still continue to recombine for some time, and so a cathodic current overshoot is observed. As a result, TiO$_2$NTs electrodes prepared at higher vol. % IL, i.e. TiO$_2$NT-2 and 4 photoelectrodes, exhibited lower surface recombination process compared to those obtained at lower vol. % IL (TiO$_2$NT-1 and 3 photoelectrodes). As a consequence of the lower surface recombination process exhibited by TiO$_2$NT-4 (observed in Fig. 5b), such photoelectrodes also exhibited higher peak photocurrent depicted by Fig. 5a and 5c, as described below.

It is possible to observe in Fig. 5a, that TiO$_2$NTs-2 and 4 electrodes exhibited a higher photocurrent compared to TiO$_2$NTs-1 and 3 photoelectrodes. One possible explanation is that higher concentration of IL leads to an increasing in the photoelectrocatalysis. Also, the photocurrent increased 30% for TiO$_2$NT-4, compared to the TiO$_2$NT-1 photoelectrode. An explanation for the increase in the peak photocurrent for higher vol. % IL TiO$_2$NTs prepared at the same anodization temperature, can be explained in light of Fig. 5b.

In order to estimate how the concentration of IL and the anodization temperature affect the photocurrent along the UV range, the photocurrent spectra are shown in Fig. 5c. It is possible to observe an increasing of 295% in the photocurrent for TiO$_2$NT-4 compared to TiO$_2$NT-1 photoelectrodes. This value is in agreement with that (i.e. 30%) obtained in Fig. 5a. This increase in the photocurrent values is related to the decrease in the surface recombination process, as discussed in Fig. 5b. All TiO$_2$NTs show a peak wavelength around 300 nm. These peak wavelength values are in agreement with the literature. Lin et al. [27] studied the strategy of doping Fe$^{3+}$ into TiO$_2$NT to enhance its photocatalytic activity. The peak photocurrent for TiO$_2$NT-Fe$_{doped}$ observed was near 325 nm. Lin et al. [28] also studied the water splitting under TiO$_2$NT with platinum nanoparticles. The authors also observed a maximum on the incident photon current efficiency on the UV-region. Augustynski et al. [29] observed a maximum in the photocurrent efficiency at 280 nm for nanocrystalline TiO$_2$ films. Finally, Jin et al. [30] studied the photoceroxidation of methanol in TiO$_2$NT, and observed a maximum in the photocurrent density near 250 nm.

Open-circuit voltage-decay (OCVD) measurements were conducted to investigate the recombination kinetics of the TiO$_2$NTs photoelectrodes. According to Kamat et al. [31], the open-circuit voltage of the photoelectrochemical cell represents the difference in Fermi level between TiO$_2$NT and counter electrodes. In the dark, the electrode potential is dictated by the redox equilibrium. Band-gap excitation of TiO$_2$ results in charge separation. As the holes are scavenged by H$_2$O at the interface, the electrons accumulate within the TiO$_2$NTs. Electrons accumulation causes a shift in the Fermi level to more negative potentials, and it reflects in an increase in the $V_{OC}$. The open-circuit voltage reaches a maximum as the electron accumulation competes with the charge recombination and this attains a steady state. Upon stopping the illumination, $V_{OC}$ decays as the electrons accumulated within the TiO$_2$NT are scavenged by acceptor species in the electrolyte (e.g. H$^+$) as well as undergo recombination with trapped holes. Thus monitoring the decay of the voltage provides an insight into the pathways by which loss of accumulated electrons occurs within TiO$_2$NT.

Following the technique as reported by Bisquert et al. [32], OCVD measurements were performed by monitoring the $V_{OC}$ transients during relaxation from an illuminated quasi-equilibrium state to the dark equilibrium, see Fig. 6-inset.

When the illumination on the TiO$_2$NT photoelectrodes is interrupted, the excess electrons are removed due to recombination, with a photovoltage decay rate directly related to the electron lifetime, by the following expression:

$$\tau = \frac{k_B T}{e} \left( \frac{\partial V_{OC}}{\partial t} \right)^{-1}$$

(2)

where the thermal energy is given by $k_B T$, $e$ is the positive elementary charge, and $\partial V_{OC}/\partial t$ is the derivative of the open circuit voltage transient. Fig. 6 is the plot of the response time obtained by applying Eq. 2 to the data in Fig. 6-inset. In general, the recombination reaction in photoelectrodes is a nonlinear property that shows a second order behaviour with respect to the electron concentration. The shape of the $V_{OC}$ curve shows a dependency on the quasi-Fermi level, confirming a trap-assisted conduction mechanism [32]. This means that the effective recombination contains contribution not only from the free carriers, but also from the trapping, detrapping and charge-transfer mechanism. Moreover, the minor delay in the electron lifetime through trapping and detrapping events is also expected considering the various TiO$_2$ crystalline phases encountered along the tubular structure of the TiO$_2$NTs. The shorter lifetimes observed at low $V_{OC}$ in Fig. 6 are related to the charge-transfer delay.

It is possible to observe also that in comparison to reported OCVD measurements, TiO$_2$NT photoelectrodes prepared at higher vol.% IL (TiO$_2$NT-2, 4 photoelectrode) exhibited longer lifetimes prepared at the same temperature anodization. Therefore, fewer recombination centers can be observed for those samples prepared using a high vol.% IL. It is important to stress out that these data corroborates different aspects: i) the higher photocurrent observed in Fig. 5a, ii) the lower cathodic current values (spike-like shape) which could then be related to a decrease in the surface recombination process (Fig. 5b), and finally, iii) higher photocurrent values observed in Fig. 5c for TiO$_2$NT-4 photoelectrode.

Aiming to investigate the photoresponse of TiO$_2$NTs photoelectrode, i-V characteristic were also carried out by linear sweep voltammetry. In order to verify that no leakage current was present, linear sweep voltammogram of TiO$_2$NT-4 photoelectrode in dark conditions are also presented in Fig. 7.

The photocurrent density of TiO$_2$NT increases with the applied potential, and almost reaches a plateau-like behaviour at 0.7 V for all TiO$_2$NTs photoelectrodes. It is possible to observe that the
onset potential and the half-wave potential (short vertical line signed) shifted 250 and 260 mV respectively, towards more negative potentials for TiO$_2$NT-4 compared to TiO$_2$NT-1 samples. The negative shift of half-wave potential indicates that, the charge separation and transportation in TiO$_2$NT-4 photoelectrodes are more efficient. Achieve a low photocurrent onset and saturation potential is important, because it reduces the applied potential required to achieve the maximum photocurrent, and thus increases the overall efficiency of water splitting. Moreover, it is possible to observe an increase in the peak photocurrent for TiO$_2$NT-4 of 130% compared to TiO$_2$NT-1 photoelectrodes. Finally, it is possible to observe that TiO$_2$NT prepared at higher vol.% IL presented higher peak photocurrent prepared at the same anodization temperature. The photoelectrocatalysis trends presented, are in agreement with those data presented in Fig. 5a, b, c and 6.

Aiming to gain information about the electronic properties of the TiO$_2$NT electrodes, AC impedance measurements were performed in the dark. It provides information about the intrinsic electronic properties of the semiconductor in contact with the electrolyte solution, as shown in Fig. 8.

Based on the Mott–Schottky plot ($1/C^2$ vs. $E$), one can extrapolate the position of the flatband potential $E_{FB}$ from the $x$-axis intercept, which is shown in Fig. 8 and Table 2. The capacitance of the semiconductor is described by the Mott-Schottky equation:

$$\frac{1}{C^2} = \left( \frac{2}{\varepsilon_0 \varepsilon_r N_D} \right) \left[ \left( E - E_{FB} \right) - \frac{k_B T}{\varepsilon_0} \right]$$

(3)

wherein $\varepsilon_0$ is the fundamental charge constant, $\varepsilon$ the dielectric constant of TiO$_2$, $\varepsilon_r$ the permittivity of vacuum, $N_D$ the donor density, $E$ the electrode applied potential, $E_{FB}$ the flatband potential, and $k_B T/\varepsilon_0$ is a temperature-dependent correction term.

As can be seen in Fig. 8, the flatband potential calculated were 1.11, 1.25, 1.2 and 1.26 V for TiO$_2$NT-1, 2, 3 and 4 photoelectrodes respectively (see Table 2), and significant change in the donor density could also be observed.

The donor density ($N_D$) is derived by the slope of the Mott-Schottky plot and is calculated via the equation:

$$N_D = -\left( \frac{2}{\varepsilon_0 \varepsilon_r} \right) \left( \frac{\partial (1/C^2)}{\partial E} \right)^{-1}$$

(4)

The donor densities were than calculated to be 6.8x10$^{18}$, 5.5x10$^{18}$, 1.5x10$^{19}$ and 1.3x10$^{19}$ cm$^{-3}$ for TiO$_2$NT-1, 2, 3 and 4 photoelectrodes respectively. It is possible to observe that TiO$_2$NTs prepared at 20 °C exhibited higher donor density compared to TiO$_2$NTs electrodes prepared at 10 °C. Schmuki et al. [33] observed that the contribution to the photocurrent from the nanotubes is related to the annealing temperature, and, the authors used the same temperature as we did here, 450 °C. The authors observed such high doping level (10$^{18}$-10$^{19}$ cm$^{-3}$) for TiO$_2$NT annealed and correlated it to the crystalline state of the material. From a different point of view, amorphous materials contain high density of recombination centers that virtually inhibit any photocurrent in the tube walls. Zhang et al. [34] studied TiO$_2$ nanorods for water splitting applications. The authors obtained donor density near 4.5x10$^{17}$ cm$^{-3}$. In comparison, Li et al. [35] obtained $N_D$ values of 2x10$^{18}$ cm$^{-3}$ for TiO$_2$ nanowires prepared by a solvo-thermal route. According to the authors, such increasing in the carrier density was attributed to a high level of defects caused by oxygen vacancies. Furthermore, in the present work, one can say that the higher was the anodization temperature employed, the greater were the oxygen vacancies observed for the material, thus, the material exhibited higher carrier. As can be observed, TiO$_2$NT-3, 4 photoelectrodes displayed higher donor density compared to TiO$_2$NT-1 and 2 photoelectrodes, prepared at 20 and 10 °C respectively.

The width of the depletion layer ($w$), can also be derived from the Mott-Schottky plot relationship and is described by:

$$w_{eff} = \left( \frac{2 e \varepsilon_0}{\varepsilon_0 N_D} \right)^{1/2} \left( E - E_{FB} - \frac{k_B T}{\varepsilon_0} \right)^{1/2}$$

(5)

A potential of 1.5 V was chosen to calculate the width of depletion layer, and the values obtained were 7.7, 6.7, 4.5 and 4.2 nm for TiO$_2$NT-1, 2, 3 and 4 photoelectrodes respectively (see Table 2). Observe that, the width of depletion layer decreases for TiO$_2$NT obtained at higher anodization temperature. Moreover, higher vol.% IL leads to decreasing in the width of depletion layer for TiO$_2$NT obtained at the same anodization temperature. Munoz et al. [36] studied semiconducting properties of TiO$_2$NT, and also observed width of depletion layer near 7 nm. Waser et al. [37,38] studied the effect of TiO$_2$ thin films preparation conditions on the width of depletion layer. According to the authors [37,38] the reduction of depletion width with increasing temperature may result from a change of charge density in the depletion region. A higher temperature can help trapped charge to be released and leave behind $N_D$ ionized sites in the depletion layer, therefore a
higher $N_D$ leads to a thinner depletion width $w$, as observed and described in data presented herein.

It is important to point out, that the TiO$_2$-NT-4 photoelectrode exhibited the lowest width of depletion layer ($w=4.2$ nm). Furthermore, such photoelectrode performed the highest photo-electrocatalysis for water splitting reaction, as already discussed in Figs. 5–7. If the film thickness is of the same order of magnitude of the width of space charge region (depletion layer). Then, most of photogenerated carriers formed inside the film reach the TiO$_2$-electrolyte interface. Grimes et al. [39] correlated sol-gel prepared 10–540 nm TiO$_2$ thin films with measured photocurrent under UV illumination. A 70 nm photoelectrode showed maximum photocurrent, nearly six times higher than those of the 180–540 nm photoelectrodes. The authors suggested that films having smaller thickness than the space charge layer show a larger photocurrent due to more effective electron-hole separation. Moreover, according to Burda et al. [22] an important question for the transport of photogenerated carriers is if the depletion layer exceeds half of the tube-wall thickness. This is important because when these photogenerated electron-hole pairs form within a layer depleted of charge carriers, the likelihood is increased that they are spatially separated and add to a measurable photocurrent [40]. Therefore, changing vol.% IL and anodization temperature it is possible to modulate the width of TiO$_2$NT depletion layer leading to an enhancement in the photocatalysis activity. Besides, in the present case, the highest photoelectrocatalysis activity observed (TiO$_2$NT-4) can be related to its lowest width of depletion layer, and consequently, to a more effective electron-hole separation.

The Debye length ($\lambda_D$) gives the spatial distance needed for an effective field screening, i.e. the distance over which significant charge separation can occur. Assuming Boltzmann statistics, the Debye length decreases with increasing concentration of carriers as:

$$\lambda_D = \left( \frac{\varepsilon \varepsilon_0 k_B T}{N_D e^2} \right)^{1/2}$$

(6)

The Debye lengths obtained were 1.4, 1.6, 0.95 and 1.0 nm for TiO$_2$NT-1, 2, 3 and 4 photoelectrodes, respectively. It is possible to observe that higher anodization temperatures decrease Debye lengths. Trapalis et al. [41] studied anatase-TiO$_2$ nanofibres, and observed Debye lengths around 1.07 and 1.64 nm for samples prepared in vacuum and in air conditions respectively. Porozet et al. [42] also studied anatase-TiO$_2$ nanoporous, and observed Debye lengths around 1.5 nm. These values are in agreement with those reported in this paper.

Lewis et al. [43] discussed the improvements of nanostructures compared to planar devices, and its relation towards water splitting reaction, such as decoupling of the direction of light absorption and charge-carrier collection. In order to design an efficient photoelectrode for water splitting applications, the absorber must be thick enough to absorb all the light, but also must be of sufficient electronic quality (i.e. purity and crystallinity) such that excited minority carriers that are photogenerated deep within the photoelectrodes are able to diffuse to surface, where they can be collected. As demonstrated above, TiO$_2$NT obtained at higher anodization temperature reduce the distance that carriers must travel, and hence enable near-unity collection efficiencies despite short minority carrier diffusion lengths. Therefore, increasing the photocatalytic activity for TiO$_2$NT-4 photoelectrode compared to others.

The decrease in the distance that carrier must travel leads to higher ability of carriers to diffuse to surface, where they can be collected. Such improvement on TiO$_2$NT prepared at higher anodization temperature, may be associated to the higher crystallite size obtained in such experimental conditions. Higher crystallite size leads to a decreasing on the density of defects (where electron-holes recombination takes place). It could also improve the diffusion coefficient, and consequently, the photoelectrocatalysis activity. Ramakrishna et al. [44] studied the improvement of electron diffusion coefficient of TiO$_2$ nanowires. According to the authors [44], enhanced particle size reduce the space charge region, thereby leading to an improved diffusion process. Low diffusion coefficients of TiO$_2$ nanoparticles can be understood by the hypothesis of electron traps in the grain boundary. Such defects could act as electron trap sites resulting from interconnection between nanoparticles. Thus, it is expected that increasing in the crystallite size could result in an improved electron transport during the water splitting reaction.

From the data described above, it is possible to conclude that it would be possible to prepare samples with different photoelectrochemical properties which are related to the synthesis variables conditions.

4. Conclusions

In summary, we have prepared TiO$_2$NT arrays photoelectrodes in ionic liquid media. Although the morphology, crystallite size and band-gap data were similar, the parameters calculated from Mott-Schottky plots revealed significant differences among the electrodes. The enhancement in the water splitting reaction obtained for the TiO$_2$NT-4 photoelectrode, seems to be linked to its small electron-hole recombination rate and, consequently, to a high electron lifetime.

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