

# Effect of Tantalum Doping on TiO<sub>2</sub> Nanotube Arrays for Water-Splitting

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## Abstract

This work is intended to define a new possible methodology for TiO<sub>2</sub> doping through the use of electrochemical deposition of tantalum directly on the titanium nanotubes obtained by a previous galvanostatic anodization treatment in an ethylene glycol solution. This method does not seem to cause any influence on the nanotube structure, showing final products with new and interesting features with respect to the unmodified sample. Together with a decrease in the band gap and flat band potential of the TiO<sub>2</sub> nanotubes, the tantalum doped specimen reports an increase of the photo conversion efficiency under UV light.

## Keywords

Nanotube, TiO<sub>2</sub>, Water Photoelectrolysis, Photoelectrode, OER

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## 1. Introduction

The publication of the fundamental work of Gong *et al.* [1], in which the authors created the basis for the development of a new synthesis model for the titania nanotubes based on the anodic oxidation of a titanium foil in fluoride based solutions, opened the way to a new methodology able to combine a simplicity of preparation of the material with a complete control of physical characteristics of the nano-system [2]-[5]. Besides, being its particular geometric shape particularly appropriate for an application as photo-anode in water-photoelectrolysis [6], many studies have been directed towards this field, which have arrived to report elevated values of UV photoconversion efficiency for these nanosystems [7] [8]. In the meanwhile, a large range of different applications for this material has been discovered. In fact, for example, it is reported that the electrical resistance of the titania nanotubes was highly sensitive to the chemisorbed hydrogen molecules hydrogen sensing [9] [10], creating a new route in the hydrogen sensing research field [11] [12]. But, many other similar examples of the wide versatility of the TiO<sub>2</sub> nanotube arrays are available in literature, as the dye-sensitized solar cells [13]-[17], li-

tium batteries [18] and also in different biological and medical researches, like the osteoblast growth [19]-[22] or drug elution [23]-[25]. As regards the application of the TiO<sub>2</sub> nanotube arrays as photo-electrodes for water photoelectrolysis, it is important to emphasize that although many important results have been reached in this field, the commercialization of such nanosystems is still far because of the high band gap of titania, which limits the light adsorption only to limited UV region [6]. So, in order to shift the light adsorption to lower energy region, many researchers focused their attention on the doping of these nanostructures. Different approaches and techniques have been used to obtain an effective doping, using nitrogen [26]-[32], carbon [33]-[37] or boron [38] [39] as doping agents. The most common procedures reported in the literature can be roughly divided into three main categories: 1) modification of the components of the anodic bath, in order to incorporate the anionic dopants during the anodization growth [29] [40] [41]; 2) thermal annealing in controlled atmosphere, using gas like pure ammonia [42] [43], dry nitrogen [44], CO [33] or H<sub>2</sub>S [45]; 3) ion implantation [27] [28]. Metal-doped semiconductors, including Ta-doped TiO<sub>2</sub>, have been widely studied for improved physical and chemical properties owing to the significant effects of the metal ion dopants on their inner electronic and/or crystalline structures [46]. It was reported that dopants with a +5 valence, such as Ta, have an ionic radius similar to that of Ti<sup>4+</sup> [47]. This dopant readily dissolves in the TiO<sub>2</sub> lattice by donating conductive electrons. Feng *et al.* [48] successfully prepared tantalum-doped TiO<sub>2</sub> nanowire arrays by a low-temperature hydrothermal method. In addition, Ta, N co-doped TiO<sub>2</sub> thin films in an anatase form were fabricated by means of a radio-frequency (RF) magnetron sputtering method [49]. In this work, we intended to describe an effect obtained by modifying the preparation of nanotubes, as proposed in previous works [8] [50], by a subsequent electro-deposition, in an organic solution containing Ta<sup>5+</sup> ions, on the lattice of the titanium dioxide.

We have found that doped titania nanotube arrays own different features with respect to the starting undoped structure. The energy gap showed to be reduced and the levels of conduction and valence band be shifted. These changes produced an increase of the photo-conversion efficiency. We retain that this methodology, if optimized and deepened, could open a new route to a best effective doping of the titania nanotube arrays.

## 2. Experimental

### 2.1. Materials and Photo-Electrode Preparation

A small disk of commercially pure grade-3 titanium (Titania, Italy) has been used as substrate for the nanotube growth. The circular sample had a diameter of 15 mm with a thickness of 0.5 mm, and was arranged to show an active circular area of 1 cm<sup>2</sup>. The un-modified sample (TiO<sub>2</sub>/Ti) was prepared with the methodology previously developed in different articles [8] [50]. Briefly, after 3 min. pickling in a HF (Carlo Erba)/HNO<sub>3</sub> (Carlo Erba) solution made by a volumetric ratio of 1:3 and diluted in deionised water until to 100 ml, the titanium disks have been set in a three-electrode cell containing a 1 M KOH solution (Carlo Erba) and subjected to a prefixed and optimized density current (1 mA·cm<sup>-2</sup>) generated by a potentiostat/galvanostat (Solartron 1286) for 3 min. The counter-electrode was a platinum sheet, while the reference was a standard calomel electrode (SCE). The anodic growth of the nanotube arrays has been obtained in a two-electrode cell with a platinum counter electrode, using a glycol ethylene (Ashland) solution with 1 %wt. H<sub>2</sub>O and 0.2 %wt. NH<sub>4</sub>F and applying 60 V for 3 h by means of a potenziostat/galvanostat PS251-2 (Aldrich). The current has been measured with a Keithley 2000 multimeter and been acquired with a Madge-Tech Volt101 digital recorder placed in series with a calibrated resistance (300 Ω) Leeds and Northrup (Figure 1).

After the anodization, the sample was washed in glycol ethylene and left overnight in a dry room. In order to transform amorphous TiO<sub>2</sub> nanotubes obtained by anodic growth into the anatase phase, which shows a higher photosensitivity, after a pre-heat treatment at 90°C in vacuum for 3 hours, the sample has been placed in a tubular furnace (Lenton) for 1 h at 580°C with a slope of 1°C·min<sup>-1</sup> in air.

After the physical and electrochemical characterizations, the same TiO<sub>2</sub>/Ti sample was doped with tantalum in order to obtaining a modified nanotube arrays Ta-TiO<sub>2</sub>/Ti. Using the Figure 1 system, tantalum's atoms have been electro-deposited on the TiO<sub>2</sub>/Ti specimen but, in this case, the TiO<sub>2</sub>/Ti has been placed as a cathode while the anode counter-electrode was a tantalum's sheet pure (5 cm<sup>2</sup>). The electrodes were placed at a distance of 1 cm in a glycol ethylene (Ashland) solution with 1 %wt. H<sub>2</sub>O and 0.2 %wt. NH<sub>4</sub>F and tantalum anode was anodized at 0.1 mA for 10 min. After the deposition the sample was washed in distilled and left overnight in a dry room. Then, the doped sample has underwent again the physical and electrochemical characterizations in order to evaluate the difference.

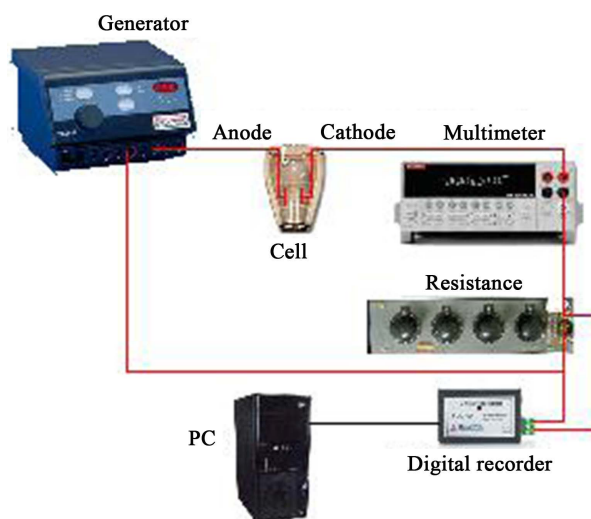


Figure 1. Scheme of anodization system.

## 2.2. Surface Analysis

The material structure was investigated with a Rigaku Miniflex diffractometer. The patterns were obtained using a Cu  $K\alpha$  radiation from a rotating anode source operating at 30 kV and 15 mA. The specimens were scanned at  $0.02^\circ \text{ s}^{-1}$  in the continuous scan mode over the  $2\theta$  range  $20^\circ - 120^\circ$ .

## 2.3. Electrochemical Measurements

The electrochemical measurements were performed using a system similar to the one described by Shankar *et al.* [7]. Briefly, it is made of a pyrex cell with a 1.5 cm diameter quartz window, where the light, emitted by UV (Ultravitalux Osram) lamp placed at distances of 4.5 cm. The source has a spectrum with peak intensity in the UVA region at 360, 400 nm and the UV intensity, which is measured on the sample by a photo-Radiometer HD2302.0 (Delta OHM) over the spectral range 220 - 400 nm, is  $24 \text{ W}\cdot\text{m}^{-2}$ . Along the optical path to the cell, a lens was interposed in order to collimate the radiation of the light source. The active surface of the sample ( $1 \text{ cm}^2$ ) was immersed in a KOH 1 M solution and placed at 0.5 cm from the quartz window (Figure 2). Photocurrents and “open circuit potential” (OCP) measurements were made via a potentiostat 1287 (Solartron). The potentiodynamic were performed with a scan rate of  $20 \text{ mV}\cdot\text{s}^{-1}$  in the range of potential  $-1.23 \div 1.70 \text{ V}$  vs. NHE in conditions of presence and absence of UV. The OCP measures were recorded in the presence and absence of UV. Impedance measurements were performed in the same cell by means of a generator of frequency response 1260 (Solartron) in the range of  $65 \text{ kHz} \div 1 \text{ Hz}$  with a sinusoidal signal of amplitude 10 mV. In particular the charging layer capacity (CSC) of the interface electrode/electrolyte was measured at a frequency of 15 kHz, applying a scanning potential of  $1 \text{ mV}\cdot\text{s}^{-1}$  between  $-1 \div 2.25 \text{ V}$  vs. NHE and with an alternating component of 10 mV in order to obtain the Mott-Schottky plot.

## 2.4. UV-Vis Absorption Spectra

The diffuse reflectance spectrum of the  $\text{TiO}_2$  samples was obtained using a Lambda 9 spectrophotometer equipped with an integrating sphere. The reflectance data was converted to the absorption coefficient  $F(R_\infty)$  values according to the Kubelka-Munk equation [51] [52]:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1)$$

The absorption coefficient  $F(R_\infty)$  and the bandgap  $E_g$  are related through the equation [53]:

$$[F(R_\infty) \cdot h\nu]^S = h\nu - E_g \quad (2)$$

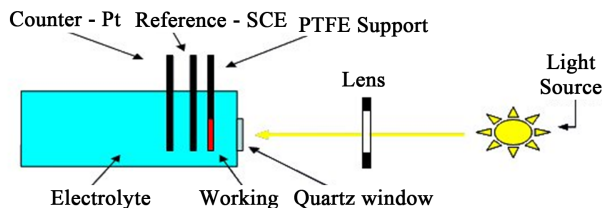


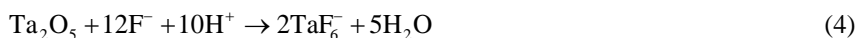
Figure 2. Experimental setup.

where  $\nu$  is the frequency,  $h$  is the Planck's constant, and  $S = 0.5$  for indirect bandgap material [6]. In this way, the plotting of  $[F(R_{\infty}) \cdot h\nu]^{0.5}$  vs.  $h\nu$ , the so-called Tauc plot, gives the possibility to obtain the optical band-gap by dropping a line from the maximum slope of the curve to the  $x$ -axis [54]-[57].

### 3. Results and Discussion

#### 3.1. Ta Doped TiO<sub>2</sub> Nanotube Arrays

The doping of the TiO<sub>2</sub>/Ti specimen is based on the evidence that, in this experimental condition, the tantalum sheet undergoes an anodization (Equation (3)) and an etching process (Equation (4)) similar to that observed for the titanium with dissolution of TaF<sub>6</sub><sup>-</sup> specie [58] [59]:



In this condition, we have a continuous Ta<sup>5+</sup> ion release in the glycol solution that can be used as doping agent for the TiO<sub>2</sub> nanotubes cathode.

It is known that, under cathodic polarization metal oxides can show significant cation in-diffusion, combined with reduction of the oxide [60]. This process is accompanied by alterations in the electronic structure of the oxide (e.g., incorporation of additional states within the band gap that change conductivity and optical properties of the material). In our case, the process could be ascribed as:



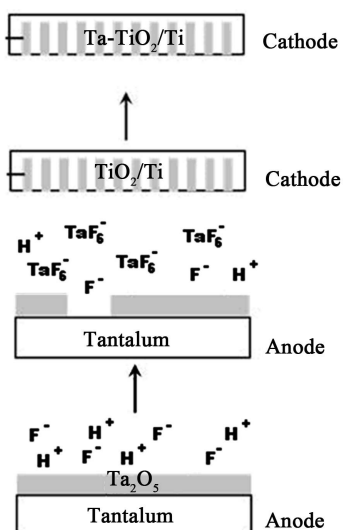
For many oxides and applied conditions this process is electrochemically reversible. Such intercalating ion uptake and release is applied for example in rechargeable batteries and switchable electrochromic devices. Obviously, the main cathode reaction is the hydrogen evolution (HER) but very few tantalum atoms can be electro-deposited onto the nanotubes surface undergoing oxidation (Equation (3)) with a mechanism like that showed in **Figure 3**.

Following this hypothesis, in TiO<sub>2</sub> lattice, under the F<sup>-</sup> etching action, titanium ions and oxide ions can deviate from their normal lattice positions, leave titanium vacancy and oxide vacancy behind. The dopant Ta, which has a 5<sup>+</sup> valence and an ionic radius similar to that of Ti<sup>4+</sup>, acts as a donor when dissolved into the TiO<sub>2</sub> lattice. So, the dissolution of Ta into the titanium oxide grains can contribute to the generation of electrons and holes for conduction which give rise to an increase of the semi-conducting behaviour [47] [61].

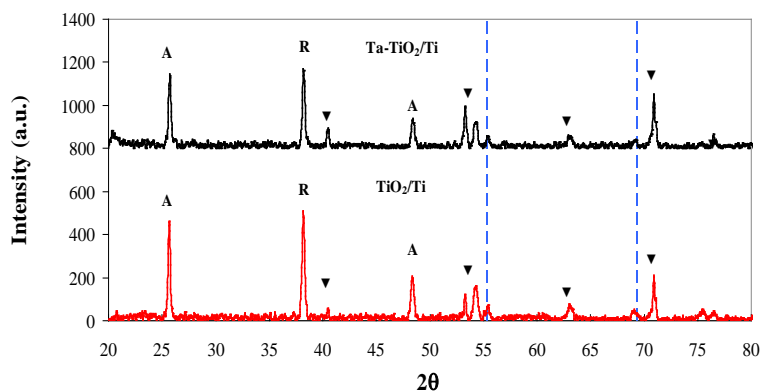
The XRD pattern of nanotube TiO<sub>2</sub>/Ti, obtained through electrosynthesis route, is depicted in **Figure 4**. From comparison with the Ta-TiO<sub>2</sub>/Ti substrate pattern (black trace), no difference can be noted and all features typical of the titanium metal and TiO<sub>2</sub> are observed. Particularly, a few peaks, ascribable to titanium oxide material anatase and rutile can be recognized [62] [63]. The results indicate that Ta doping does not introduce changes in the TiO<sub>2</sub> structure.

#### 3.2. Analysis of the Absorbance Spectra

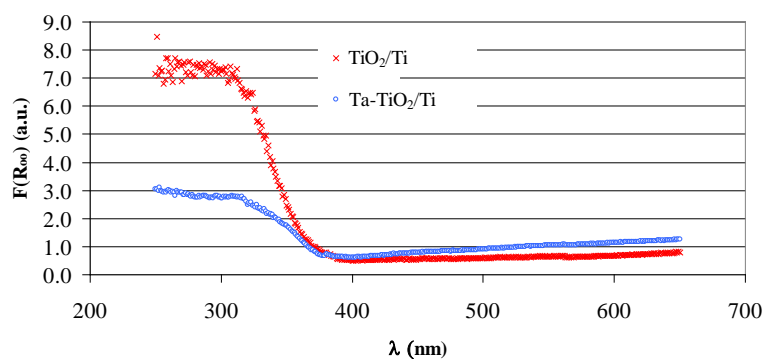
The diffuse absorbance spectra of the two samples, obtained by the Kubelka-Munk equation, are showed in **Figure 5**. Both the samples show the main absorbance in the UV range of 300 - 350 nm, but the TiO<sub>2</sub>/Ti sample owns a better behavior in this part of the spectrum. Instead, the Ta-TiO<sub>2</sub>/Ti specimen shows an increase in the low UV region, starting from a wavelength of 380 nm.



**Figure 3.** Schematic representation of the reaction leading to the Ta doping.

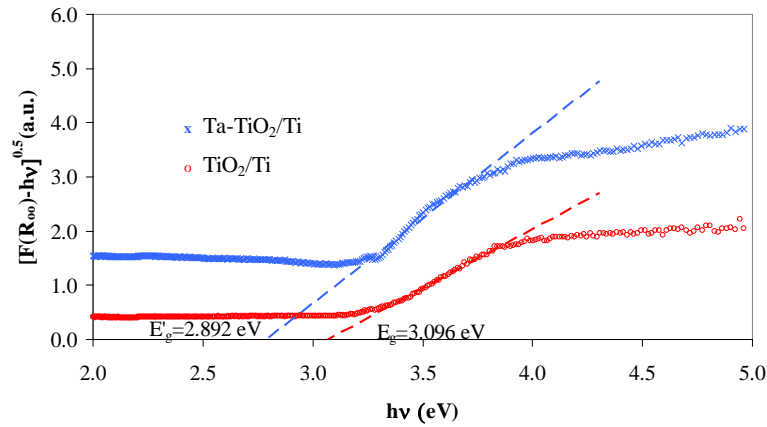


**Figure 4.** XRD pattern of nanotube TiO<sub>2</sub>/Ti and Ta-TiO<sub>2</sub>/Ti obtained through electro-synthesis route; (A) anatase, (R) rutile, (▼) titanium. The dashed lines indicate the Ta position [63].



**Figure 5.** Diffuse reflectance spectra of the TiO<sub>2</sub>/Ti (×) and Ta-TiO<sub>2</sub>/Ti (○) according to the Kubelka-Munk equation.

The band gaps of the two samples are calculated using the Tauc plot (**Figure 6**), as previously described. The result of this operation shows a decrease of the Ta-TiO<sub>2</sub>/Ti band gap of about 0.204 eV with respect to the normal titania nanotube arrays.



**Figure 6.** Transformed Kubelka-Munk function vs. energy of excitation source for  $\text{TiO}_2/\text{Ti}$  ( $\times$ ) and  $\text{Ta-TiO}_2/\text{Ti}$  ( $\circ$ ).

### 3.3. Analysis of the Photo-Electrochemical Performance

**Figure 7** shows the open circuit potential ( $E_{ocv}$ ) for  $\text{TiO}_2/\text{Ti}$  and  $\text{Ta-TiO}_2/\text{Ti}$  with UV on and off. When applying the UV,  $E_{ocv}$  decreases sharply and it reaches a steady state at a lower potential. After the switching off the light source,  $E_{ocv}$  increases rapidly in the first seconds and then slowly until to a new steady state level. In UV on condition, the doped electrode shows an  $E_{ocv}$  of  $-0.68$  V vs NHE while the un-doped one  $-0.57$  V. The decrease of photo-potential indicates a clear effect on the degree of band bending for the doped n-type metal oxide semiconductor.

**Figure 8** shows the curves of photo-current and photo-electrochemical performance of  $\text{TiO}_2/\text{Ti}$  and  $\text{Ta-TiO}_2/\text{Ti}$ . The photo-conversion efficiency  $\eta$ , which is the light energy to chemical energy conversion efficiency, is calculated as [7]:

$$\eta(\%) = i_{ph} \frac{[E_{rev}^o - |E_{app}|]}{J_o} \times 100 \quad (6)$$

where  $i_{ph}$  is the photocurrent density ( $\text{mA}\cdot\text{cm}^{-2}$ ),  $i_{ph}E_{rev}^o$  is the total power output,  $i_{ph}|E_{app}|$  is the electrical power input and  $J_o$  is the power density of incident light, which is  $2.4 \text{ mW}\cdot\text{cm}^{-2}$ .  $E_{rev}^o$  is the standard reversible potential of 1.23 V/NHE. The applied potential can be calculated:

$$E_{app} = E_{meas} - E_{ocv} \quad (7)$$

where  $E_{meas}$  is the electrode potential (versus NHE) of the working electrode, at which photocurrent was measured under illumination,  $E_{ocv}$  is the electrode potential (versus NHE) of the same working electrode at open circuit conditions under the same illumination and in the same electrolyte.

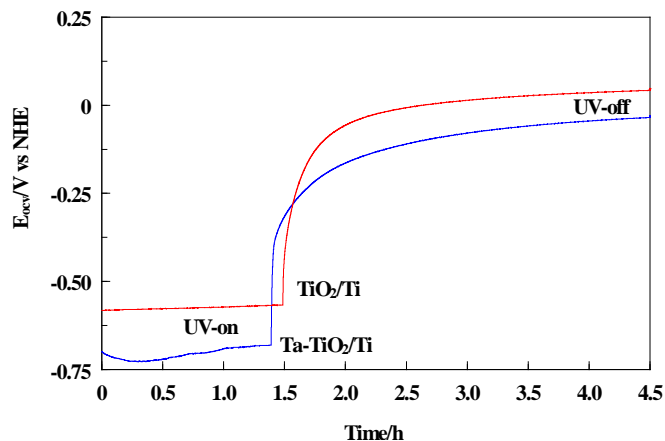
After doping, the efficiency of photo-electrochemical rose from 8% to 12% with an increase in photocatalytic activity by 49%. The onset photo potential for the discharge of water  $E''$  moves to more negative values from  $-0.68$  to  $-0.84$  V vs. NHE. In contrast, the potential onset of  $E'$  remains almost unchanged at approx. 0.77 V vs. NHE. At the same time, however, it has a supplementary reduction of the catalytic activity of 40% shown by the reduction of current for higher potential to 1.25 V.

The flat band potential  $E_{fb}$  has been determined for both electrodes from the photocurrent measurements applying the equation [64] [65].

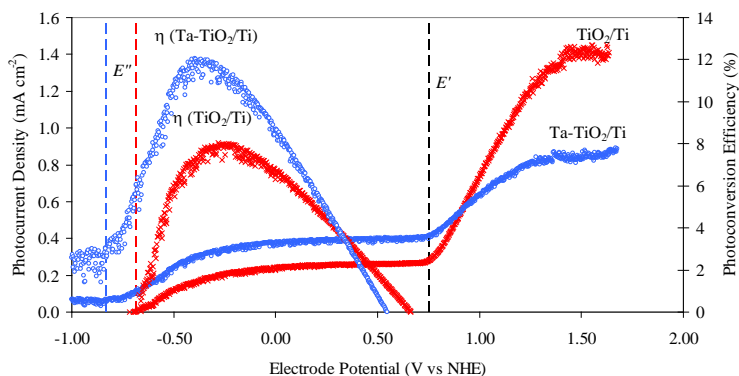
$$i_{ph}^2 = \left( \frac{2\varepsilon_r \varepsilon_0 e \alpha J_o}{N_D} \right) (E_{meas} - E_{fb}) \quad (8)$$

where  $N_D$  denotes the donor density,  $\varepsilon_r$  the relative dielectric constant of the  $\text{TiO}_2$  anodic film (55) [66],  $\varepsilon_0$ , the vacuum permittivity ( $8.86 \times 10^{-14} \text{ F}\cdot\text{cm}^{-1}$ ),  $e$  the charge of an electron ( $1.602 \times 10^{-19} \text{ C}$ ), and  $\alpha$  the light absorption coefficient for the material.

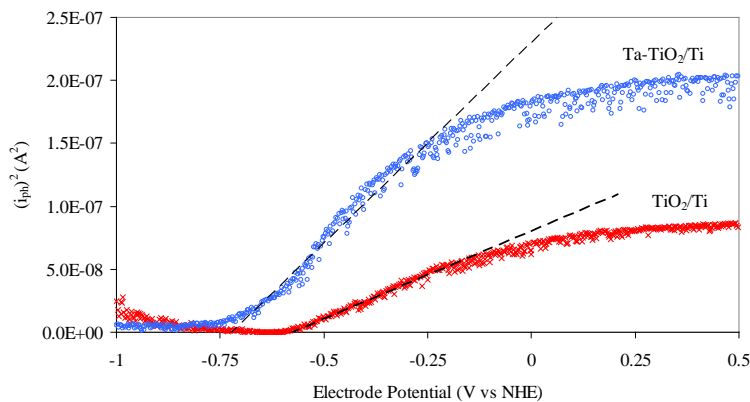
The  $E_{fb}$  calculated in the **Figure 9** as the intercept with the abscissa, decrease for Ta doped of about 22% from  $-0.56$  to  $-0.72$  V vs. NHE thus indicating a possible change in the semiconductor electronic structure.



**Figure 7.** Open circuit potential at UV on and off for TiO<sub>2</sub>/Ti (red) and Ta-TiO<sub>2</sub>/Ti (blue).



**Figure 8.** UV photocurrent density and efficiency vs. voltage for TiO<sub>2</sub>/Ti (x) and Ta-TiO<sub>2</sub>/Ti (o).



**Figure 9.** Square photocurrent vs. electrode potential for TiO<sub>2</sub>/Ti (x) and Ta-TiO<sub>2</sub>/Ti (o).

The slope of the so-called Mott-Schottky plots allows calculation of the donor density [67]-[70]. The change of the n-semiconductor doping density  $N_D$  can be estimated using the Mott-Schottky relationship in the linear part of diagram by the equation [66] [67]:

$$N_D = \frac{2}{ke\varepsilon_r\varepsilon_0} \quad (9)$$

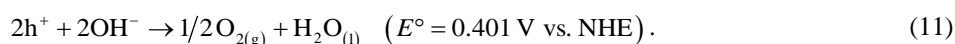
where  $k$  is the slope of  $(1/C_{sc})^2$  vs. electrode potential plot. **Figure 10** shows the Mott-Schottky plot for  $\text{TiO}_2/\text{Ti}$  and  $\text{Ta-TiO}_2/\text{Ti}$ , evidencing a clear decrease of the  $k$  slope after the Ta doping with a calculated  $N_D$  increase from  $1.3 \times 10^{27} \text{ m}^{-3}$  to  $2.4 \times 10^{27} \text{ m}^{-3}$ .

All the photo-electrochemical characteristic of  $\text{TiO}_2/\text{Ti}$  and  $\text{Ta-TiO}_2/\text{Ti}$  are summarized in **Table 1**.

In considering light receptor electrodes for photo-electrochemical cells an important criterion is the absolute position of the valence ( $VB$ ) and conduction bands ( $CB$ ). In fact, fast electron transfer across the electrolyte semiconductor interface occurs when the appropriate band overlaps the redox level of the electrolyte. This is important since recombination of the photo-generated electron-hole pair competes with the electron transfer, and thus these relative rates influence quantum efficiency. The absolute position of the bands effectively controls the degree of band bending,  $E_B$ , since the surface Fermi level,  $E_F$ , for the heavily doped n-type metal oxide semiconductor approximately coincides with the  $CB$  level. The value of  $E_B$  is generally taken as the difference between  $E_F$  and the ‘‘Fermi level’’ of the electrolyte which is taken as the redox potential,  $E_{redox}$  for the reaction occurring at the photo-electrode [69]:

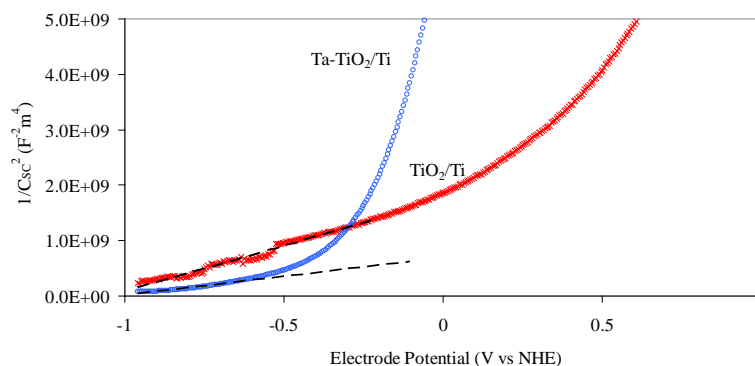
$$E_B = E_F - E_{F-Redox} \quad (10)$$

for water oxidation in alkaline media (Equation (9)) and for  $\text{TiO}_2/\text{Ti}$  n-type semiconductor photo-electrodes  $E_{redox}$  is the  $\text{O}_2|\text{OH}^-$  potential:



The maximum open-circuit photo-potential is  $E_B$  and if it exceeds 1.23 V, then it is possible to run water splitting without any other energy source other than the light. To the extent that  $E_B$  falls short of 1.23 V (plus any required overvoltage) one requires an additional energy input assisting the effect; an applied potential,  $V_{app}$ , must be supplied to provide the difference. Since  $E_F = E_{CB}$  for the materials of interest here, we can conclude from this discussion that the  $CB$  position must be 1.23 V above the  $\text{O}_2|\text{OH}^-$ . This analysis evidence that Ta doping shift the absolute position of the valence and conduction band so increasing the  $E_B$  value and reducing the overvoltage required for water splitting.

The increase of donor density justify the shift of energy levels. The position of the Fermi level lies between the valence and conduction bands, it is dependent on the electron accumulation within the semiconductor particles. So, the main Ta doping effect is to accumulate more electrons/holes within the semiconductor structure and following the band gap excitation, the Fermi level becomes more negative and shifts closer to the conduction-band edge [71].



**Figure 10.** Mott-Schottky plots for  $\text{TiO}_2/\text{Ti}$  ( $\times$ ) and  $\text{Ta-TiO}_2/\text{Ti}$  ( $\circ$ ).

**Table 1.** Photo-electrochemical characteristic of  $\text{TiO}_2/\text{Ti}$  and  $\text{Ta-TiO}_2/\text{Ti}$  anodes.

Sample	$E_{OCV} \text{ V}^\#$	$\eta \%$	$i_{ph}^* \mu\text{A cm}^{-2}$	$E_{FB} \approx E_{CB} \text{ V}^\# (\text{eV})$	$E_{VB} \text{ V}^\# (\text{eV})$	$E_B \text{ V}^\# (\text{eV})$	$N_D \text{ m}^{-3}$
$\text{TiO}_2/\text{Ti}$	-0.57	8.03	285	-0.59 (-4.01)	2.28 (6.88)	-0.99	$1.3 \times 10^{27}$
$\text{Ta-TiO}_2/\text{Ti}$	-0.68	12.04	446	-0.72 (-3.88)	2.07 (6.67)	-1.12	$2.4 \times 10^{27}$

$^\#$ V vs NHE;  $^*$  measured at 0.241 V vs. NHE.



## 4. Conclusion

In this work, we have reported a preliminary study for a new possible doping route for anodic titania nanotubes. This methodology, yet to be improved and optimized, shows as a first positive feature the fact that the presence of a Ta ions into the TiO<sub>2</sub> nanotubes can produce relevant changes in the electronic structure. Besides, this technique leads to a decrease in the TiO<sub>2</sub> band gap and an improvement of the ability of the titania nanotubes to use UV radiations of lower energy.

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