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Application of Taguchi Method to Study Morphological Evolution of TiO_2 Nanotubes Obtained Via Anodization Process

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The growth of titanium dioxide nanotubes (TiO_2) via anodization process depends on the controlling parameters such as applied potential, anodization time, and electrolyte composition. In the present work, the Taguchi method was applied to evaluate statistically the influence of the anodization parameters on the morphology of anodized TiO_2 films. Mixture of ethylene-glycol and glycerol was used as an electrolyte and the settings of the experimental design were parameterized on the basis of four important anodization factors consisting of chemical pretreatment, amount of fluoride, water content and applied potential. Samples were characterized by XRD and FEG-SEM. Based on 4 variables at 3 different settings, full factorial plan requires $3^4 = 81$ tests. In this work the experiment was designed on the basis of an L9 (3^4) orthogonal array (4 variables, 3 levels, 9 tests). The optimum conditions were found on the basis of *smaller-is-better* and *larger-is-better* analyses. The signal-to-noise ratio was employed to find optimal process parameters levels and to analyze the influence of these parameters on the tubular length, internal and external diameters and formation of nanograss on the film surface. Hence, it is clearly shown that the performance of TiO_2 nanotubes can be evaluated by the Taguchi method.

Keywords: *Titanium dioxide nanotubes, Taguchi method, Anodization, Parameters.*

1. Introduction

Titanium dioxide TiO_2 based nanostructures are widely used in solar cells[1,2], hydrogen production[3], sensors[4], photocatalysis[5-7], effluent treatment[8,9] and biomedical applications[10]. TiO_2 nanoarchitectured morphologies can be synthesized through various techniques[11,12]. Anodization is one widely used technique that is simple and provides a precise control over the syntheses of nanomorphologies[5,13,14]. Based on its large surface area, TiO_2 nanotubular morphology synthesized via the anodization process is promising for its potential applications such as in photocatalytic and photovoltaic devices[12,13]. Anodization in fluorinated electrolytes is one effective method employed to obtain highly ordered nanotube arrays of TiO_2 and many other materials with controllable morphologies[1]. The uses of organic electrolytes with different concentrations of water and fluoride salts have been widely reported[15]. These electrolytes are less aggressive and offer better efficiency to obtain highly ordered nanotubular arrays[12,16,17].

In the anodization process there are many factors that have significant influences on the morphology of TiO_2 nanotubes[18], e.g. pretreatment of the Ti substrate[19], NH_4F concentration[20], percentage of H_2O contained in the electrolyte[21], anodization potential[18,22], electrolyte viscosity[23], anodization temperature[24], mixture of electrolytes[18,21] and anodization time[18,25]. A few examples below can elaborate their effects; electrolytes consisting of ethylene glycol[26] enable thicker oxide layers as compared to the electrolyte composed of only glycerol[21,27].

Recently, we have synthesized TiO_2 nanotubes in the mixture of glycerol and ethylene glycol and found that the double wall features of the nanotubes can be controlled by the anodization time[18]. Bervian et al.[28] have shown that the length of the TiO_2 nanotubes increases with increasing anodization time; however, the diameter of the nanotubes was not changed. In addition, there is a linear relationship between the diameter of the nanotubes and the anodization potential.

Xie et al.[24] observed that at low NH_4F concentrations a continuous layer, containing some pits, forms on the top of nanotube arrays of TiO_2. However, for the higher NH_4F concentration the continuous layer on the nanotubes was not observed. Xue et al.[15] reported that the average internal nanotubes diameter increased with the increase of NH_4F

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concentration. To optimize the growth of nanotubes it is necessary to evaluate the influence of these factors. Changing all these multiple parameters simultaneously is technically expensive, very laborious and time-consuming. Therefore, it is promising to use a statistical model that can help to find the best operating parameters to obtain highly ordered TiO_2 nanotubular arrays with the desired geometrical features including length, diameter and wall thickness.

Statistical design of experiments refers to the process of planning the experiment so that appropriate data can be collected and analyzed by statistical methods, resulting in valid and objective conclusions. Design of Experiment (DOE) focuses on choosing the levels of controllable factors (or parameters) to ensure that the mean of the output response is at a desired level or target and to ensure that the variability around this target value is as small as possible. The number of experiments in a DOE depends on the number of levels and controlling factors[28,29].

The Taguchi experimental model is a robust statistical method that minimizes the number of variations in the experiments and has been widely used in industry to improve the quality of products[30,31]. The Taguchi approach to DOE considers an orthogonal array of factors to reduce the number of experiments involved in the process of optimizing the activities. It is also a simple and efficient technique in research to investigate the effects of multiple factors, employing the best parameters[32,33]. The Taguchi method is a combination of mathematical and statistical techniques used in an empirical study[34].

Instead of testing all possible combinations as a planning factorial experiment, this method allows the collection of only the required data with the minimum possible experimental activities, thereby saving time and research resources. Furthermore, the Taguchi approach identifies some types of factors that cause variability in the important system response variables. These noise factors are often functions of environmental conditions such as temperature or relative humidity. Zhu et al.[32] applied Taguchi design to optimize the degradation phase parameters of TiO_2 composite photocatalysis. Ghani et al.[34] have shown that the Taguchi method is suitable to solve the stated problem with the minimum number of trials as compared with a full factorial design.

Taguchi statistical experiments were carried out to determine the influence of the morphology variables of the TiO_2 nanotubes. Since in the anodization process there are multiple process parameters that influence the morphology of the anodized film. It is therefore promising to study the influence of these parameters on the morphological evolution of TiO_2 nanotubes applying the Taguchi method. This study aims apply the L9 orthogonal array because reduces considerably the experiments[35,36].

As reported in the literature[18,21,37,38] several parameters influence the formation of TiO_2 nanotubes. Thus, it was studied parameters that have a great influence on the development of morphology of the TiO_2 nanotubes which requires greater attention, as: chemical pre-treatment, ammonium fluoride concentrations, water content and applied potential.

The objective of this study via anodization process in a mixture of ethylene glycol and glycerol is to evaluate their influence on the tubular length, internal and external diameters and formation of nanograss on the film surface following the Taguchi method and aiming to obtain highly ordered TiO_2 nanotubes.

2. Experimental

2.1 Materials and sample preparation

Nanotubes were grown on Ti foil grade 2 - ASTM-F67 (99.8 wt.% purity, 0.7 mm thickness, Realum), with dimensions of 1 cm × 5 cm. These foils were cleaned by ultrasonication for 15 minutes in degreasing agent and deionized water (DI) in sequence and dried under cold air. Anodization was carried out in an electrochemical cell with a two-electrode configuration and with a Minipa MPC 303 DI power supply controlled by TCXX. In the anodizing system, the Ti foil was used as a working electrode and a platinum foil was used as a counter electrode. The distance between the electrodes was fixed at 2 cm[37]. The anodization was performed without stirring and applying 20, 40 and 60 V at a potential ramp of 1 Vs^{-1}. The organic electrolyte was a mixture of glycerol (Synth 99.5%) and ethylene glycol (Synth - purity: 99.0%) in 3:1 (v/v) ratio[18]. The mixture composed of ethylene glycol and glycerol was adopted due to the influence of the geometry of the formed nanotubes. The concentration of ammonium fluoride (NH_4F) was 0.25, 0.50 and 0.75 wt.% (Synth - purity: 98.0%) and the concentration of the deionized water was 0, 2 and 10 wt.%.

The pH was measured prior to NH_4F addition at the organic electrolyte with a pH meter organic (Mettler Toledo HA405-60-88G-S7/120). The pH obtained was 7.8. Also was measured with the pH test strips (Acilit® pH 0-6; Merck) obtaining in the range pH 5-5.5. After addition of NH_4F at the organic electrolyte the pH was measured only with pH test strips, and found to in the range pH 4.5-5. The time of anodization employed was 180 minutes at room temperature (23 ºC ± 2 ºC) and the viscosity of the mixture was 104.6 Pa s. The current transient (I-t) curves were obtained by using a system acquisition of data (Multimeter Minipa ET-2076A) recorded from the source meter connected with software TCXX. After anodization, the samples were annealed in a muffle furnace at 450 °C for 3 h with a heating ramp of 10 ºC min^{-1} to crystallize the TiO_2 nanotubes[39,40].

2.2 Taguchi method design of experiment

In this work, a standard Taguchi experimental plan L9 was chosen to optimize the experimental conditions to evaluate the morphology of the TiO_2 films prepared by the anodization process in a mixture of ethylene glycol and glycerol. Four essential process parameters were chosen for this study: Ti chemical pretreatment, concentration of water, NH_4F concentration and the applied anodizing potential. The variation of these factors in turn was based on three different levels: 1) low, 2) medium and 3) high, as shown in Table 1.

With the aim of taking into account the highest degree of interaction, a fully balanced factorial plan was implemented. Thus, a simple factorial design was applied to assign three levels for each parameter and the numbers of permutations would be 8, i.e., degrees of freedom = 9-1 = 8. However, the fractional factorial design reduced the number of experiments to 9. This is shown in Table 2. The choice of parameters was based on the fact that these are the parameters that show the most influence in the anodization process, according to the results mentioned in the literature[37,38]. Table 2 represents the Taguchi orthogonal array (L9)[41]. And the ranking was assigned on the basis of the parameters shown in Table 1.

The most important guidelines that support this method are the orthogonal arrays (L9) and the signal-to-noise (S/N) ratios, which are derived on the basis of loss functions that penalize even small deviations from the target performance level. The first ones allow one to design an optimal plan from a minimum number of experiments, and the S/N ratio makes it possible to estimate the variability of the system response in terms of controllable parameters and random signals[33].

There are three types of S/N ratios used in the Taguchi method and these are *nominal-is-best*, *smaller-is-better* and *larger-is-better*[32,41]. In this study, it is necessary to calculate the signal-to-noise (S/N) ratio for each experiment and thus determine the effect that each variable has on the output. The S/N for the length of the nanotubes is calculated according to the equation *smaller-is-better* Equation 1, aiming to maximize the S/N ratio. For the S/N ratios of the internal diameter (nm) and external diameter (nm) of the TiO_2 nanotubes, the *larger-is-better* theorem evaluated from Equation (2) is used[32,42,43,44]:

$$SN_L = -10\log\left[\frac{\sum_{i=1}^{n} yi^2}{n}\right] \tag{1}$$

$$SN_L = -10\log\left[\frac{\sum_{i=1}^{n} 1/yi^2}{n}\right] \tag{2}$$

where: n is the number of variables and y_i is the value of each variable. The samples mentioned in Table 2 are labeled as Exp. 1 to Exp. 9 from top to bottom, respectively of the first column.

2.3 Characterization

The TiO_2 crystalline structure was determined by X-ray diffraction (XRD) using an XRD-6000 by SHIMADZU, operated at 40 kV and 30 mA. The X-ray source consists of Cu radiation (1.54184 Å) selected with an Ni filter. The measurements were performed with a step of 0.05° and a counting time of 0.60 seconds per step and θ/2θ geometry was used. The cross-section morphology was evaluated by the images obtained by Field Emission Gun Scanning Electron Microscope (FEG-SEM) equipment MIRA3 by TESCAN operated at 10 and 15 kV. The micrographs of

Table 1. Process parameters with their different observation levels

		Variables levels		
	Parameters	1 Low	2 Medium	3 High
A	Chemical pretreatment	No treatment	1 min	5 min
B	Concentration of water	No water	2 wt.% H_2O	10 wt.% H_2O
C	Applied potential	20 V	40 V	60 V
D	Concentration of NH_4F	0.25 wt.%	0.50 wt.%	0.75 wt.%

Table 2. Orthogonal array (L9) proposed by Taguchi method to study the variation of four parameters in 3 different levels and the obtained experimental results during 180 minutes of anodization

Sample	Variable parameters			
	Chemical pretreatment	Concentration of water	Applied potential	Concentration of NH_4F
1 - $A_1B_1C_1D_1$	1	1	1	1
2 - $A_1B_2C_2D_2$	1	2	2	2
3 - $A_1B_3C_3D_3$	1	3	3	3
4 - $A_2B_1C_2D_3$	2	1	2	3
5 - $A_2B_2C_3D_1$	2	2	3	1
6 - $A_2B_3C_1D_2$	2	3	1	2
7 - $A_3B_1C_3D_2$	3	1	3	2
8 - $A_3B_2C_1D_3$	3	2	1	3
9 - $A_3B_3C_2D_1$	3	3	2	1

the surface and cross-section of the nanotubes were taken at various magnifications.

The main effect is observed for each parameter in the plot analyzed by MINITAB. The lengths, internal and external diameters of the obtained structures were determined using the software Image J.

3. Results and Discussion

The as-anodized TiO_2 nanotubes are generally amorphous; therefore, thermal treatment was required to crystallize them. Fig. 1 shows the XRD patterns of the samples annealed at 450 ºC for 3 h. The characteristic peak related to the anatase phase of TiO_2 appears at 2θ = 25.2º, i.e., in agreement with the standard JCPDS No. 89-4921. The diffractograms of the samples do not present any peak assigned to rutile phase that normally appears at 2θ = 27.36º[45]. Hence, the samples prepared in this work consist of anatase crystalline phase. The peaks at 38.3º, 40.4º and 53.4º correspond to the Ti substrate. For Exp. 4 and Exp. 7, it can be observed that the relative peak intensity at 37.8º corresponding to the (004) plane of anatase phase slightly increases as compared to other samples[44,46,47].

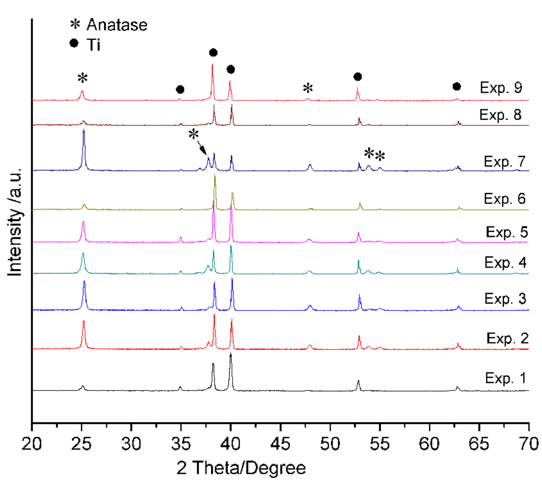

Figure 1. XRD patterns of TiO_2 samples for different experiments (Table 2) annealed at 450 °C for 3 h

Fig. 2 displays the FEG-SEM cross-sectional images of the heat treated films and their thicknesses are displayed in Table 3. It can be observed that Exp. 1 and Exp. 6 present a relatively thinner oxide layer as compared to other experiments (Table 3); however, Exp. 1 does not present a tubular morphology. It should be noted that both samples were obtained at lower applied potential level (Table 2). The oxide thicknesses for Exp. 2, Exp. 3 and Exp. 4 were 2.51 µm, 2.70 µm and 2.80 µm, respectively (Table 3). The sample in Exp. 8 shows the formation of a discontinuous and completely irregular nanostructure without formation of nanotubes. Exp. 5 and Exp. 7 resulted in the smoothest and longest nanostructure (4.72 µm and 7.66 µm, respectively). Among all the samples, smooth walls were obtained for Exp. 4, Exp. 5 and Exp. 7. The S/N ratio of aspect ratio and standard deviation of TiO_2 nanotubes for 9 experiments are calculated as shown in Table 3. Then, the S/N ratio response to each factor at each level were obtained from the orthogonal array experiments which calculated from the average S/N ratio for each level of the factors[32,43].

As illustrated in Table 3, Exp. 3 ($A_1B_3C_3D_3$) has value internal diameter higher of S/N 41.61 with the average nanotubes internal larger and standard deviation at 115.4 ± 22 nm. However, Exp. 6 ($A_2B_3C_1D_2$) with the S/N value of 31.38 and the smaller internal diameter and standard deviation at 38.2 ± 3 nm. Therefore, for the external diameter it is observed that Exp. 3 shows the largest diameter external and Exp. 6 the smallest external diameter. Thus, it can be concluded that the Exp. 3 is a strong candidate for application in the photocatalytic decomposition in formaldehyde and methylene blue[47,48]. However, for the thickness of the TiO_2 nanotubes it is observed (Table 3) that the higher the thickness of the nanotubes the higher the S/N.

As mentioned before, the signal-to-noise (S/N) ratio analysis is adapted to improve the statistical properties of the Taguchi design method used in this work to evaluate the conditions required to obtain ordered TiO_2 nanotubular arrays by anodization (Fig. 3). In this study, for measurable quality characteristics, the equation *smaller-is-better* was used as in Eq. (1)[32].

In the Fig. 3, Fig. 5 to Fig. 7 for the parameters the chemical pretreatment (A) and water concentration (B) the level 1 means that the lower level of chemical treatment was performed in time equal to zero, it means without any chemical attack, and for parameter B (water concentration) there was no addition of water in the organic electrolyte. Therefore, level 1 was chosen in this way to verify their behavior/influence of these variables in all processes of the production of TiO_2 nanotubes.

Fig. 3 shows the S/N ratios calculated from Eq.(1) for different lengths of the TiO_2 nanotubes (Table 3). Optimal levels obtained from S/N ratios are marked on the graphs with a circle. This parameter (*smaller-is-better*) was chosen because, according to the literature, it is reported that shorter TiO_2 nanotubes had a better efficiency in degradation of pollutants and hydrogen production, compared to longer nanotubes[18,49]. The longer nanotubes have a slower internal diffusion for reactants, which is detrimental to the reaction rate[12,49]. The Taguchi orthogonal array (L9) is an approach to reduce the number of experiments optimizing the parameters and the response variable as reported in the literature[30,41].

Therefore, by means of the Fig. 3, it is possible to see that the studied parameters ((A) chemical pretreatment, (B) concentration of water, (C) applied potential and (D) concentration of NH_4F) influence in the following order (from larger to smaller importance) when the objective is to

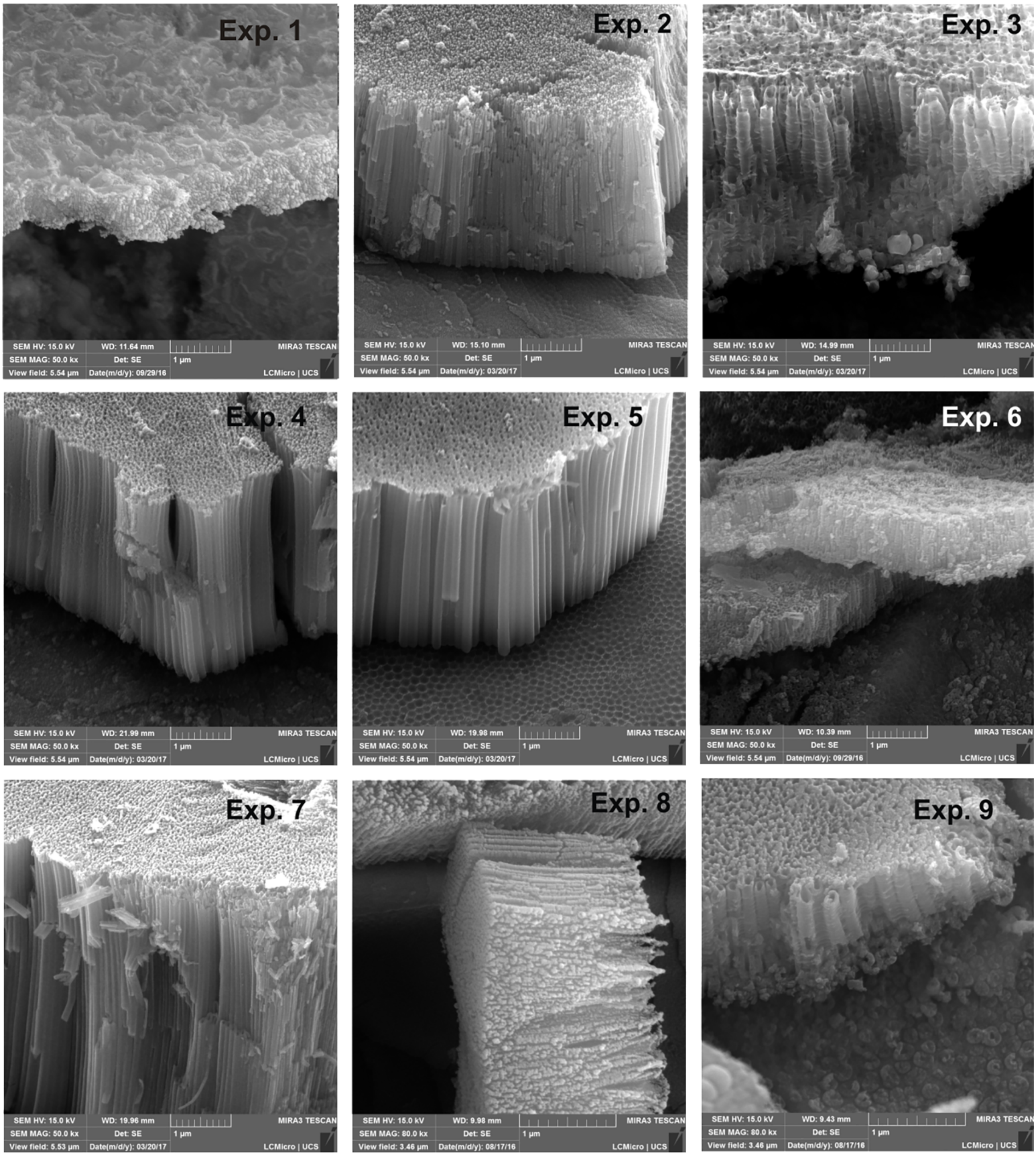

Figure 2. Cross-sectional images obtained by FEG-SEM of TiO_2 nanotube arrays fabricated for 180 minutes of anodization and annealed at 450 °C for 3 h

obtain smaller nanotubes: applied potential, concentration of water, concentration of NH_4F and chemical pretreatment. So to get smaller nanotubes what should be taken into account is the ranking described above.

Fig. 4 shows the top-view FEG-SEM images of the heat treated samples and the external and internal diameters are displayed in Table 3. It can be observed that Exp. 1 (Fig. 4) presents no formation of nanotubes. However, the presence of the oxide on the surface can be observed from the cross-sectional view (Fig. 2), which clearly identifies that the formation of the TiO_2 nanotubes did not occur. For Exp. 4 and Exp. 7 is observed cracks in top. In the literature[20,50,51] reports that these cracks can be caused by various forms, such as through the from chemical and field-assisted dissolution of the oxide at local points of high energy, or through the capillary force that appears when solvent rapidly evaporate from film surface during drying process of the TiO_2 nanotubes, decreasing of bond strength among TiO_2 nanotubes when the film is thick.

It is also evident that after 180 minutes of anodization, there is a compact oxide region on the top of these samples, called nanograss[52]. Thus, the tubular structure of the nanotubes

Table 3. Mean values of internal diameter, external diameter and thickness of the heat treated layer and their respects signal-to-noise (S/N) ratio

Sample	Internal diameter (nm)	S/N ratio for internal diameter	External diameter (nm)	S/N ratio for external diameter	Average thickness deviation (µm)	S/N ratio for thickness
1 - $A_1B_1C_1D_1$	---	-55.75	---	-55.75	0.75 ± 0.1	-2.48
2 - $A_1B_2C_2D_2$	46.6 ± 4	33.69	83.0 ± 7	38.37	2.51 ± 0.1	7.97
3 - $A_1B_3C_3D_3$	115.4 ± 22	41.61	205.4 ± 25	46.22	2.70 ± 0.2	8.76
4 - $A_2B_1C_2D_3$	35.0 ± 6	30.61	93.0 ± 9	39.27	2.80 ± 0.1	5.08
5 - $A_2B_2C_3D_1$	51.0 ± 7	33.60	195.2 ± 15	44.20	4.72 ± 0.7	13.12
6 - $A_2B_3C_1D_2$	38.2 ± 3	31.38	69.5 ± 6	37.05	0.88 ± 0.1	-1.32
7 - $A_3B_1C_3D_2$	41.4 ± 8	31.95	108.7 ± 5	40.73	7.66 ± 0.3	17.76
8 - $A_3B_2C_1D_3$	---	13.45	---	33.45	1.81 ± 0.1	5.42
9 - $A_3B_3C_2D_1$	49.00 ± 10	33.18	89.4 ± 17	38.54	1.15 ± 0.1	1.19

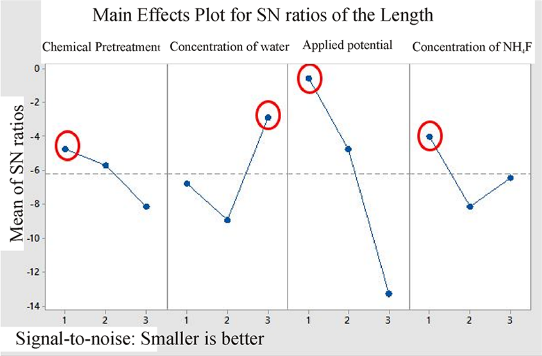

Figure 3. The trend diagram of each parameter on the mean for the length of the nanotubes (signal-to-noise (S/N) ratio)

could not be visualized, but only the presence of very open pores can be observed, indicating that the nanograss is covering the top of the nanotubes[53]. For Exp. 2, Exp. 3 and Exp. 6 the top surfaces clearly present tubular structures. In Exp. 5 (Fig. 4) the top is covered with nanograss and after removal of the surface oxide, the top-view image clearly shows that these nanotubes are composed of well-defined inner and outer shells.

According to the literature[12,54,55,56], nanograss on the surface of TiO_2 nanotubes is undesirable, and for this reason it is important to obtain nanotubes free of nanograss. Using the *smaller-is-better* criterion levels for the operating parameters of the nanograss on top of TiO_2 nanotubes, the S/N ratio was obtained from Eq. (1)[32]. The criterion adopted to determine the presence of the nanograss was by percentage of covered surfaces, with values of 10, 50 and 100% being assigned according to the amount that covered the surface of the sample. The 10% value corresponds to samples with free or low amount of nanograss. The 50% value corresponds to the surface of the sample with approximately half of the surface covered with nanograss and the value 100% percent corresponds to the samples completely covered by this oxide.

It can be seen that the studied parameters influence in the following order (from more to less important) as shown in Fig. 5, when the objective is to obtain nanotubes free of nanograss: (A) chemical pretreatment, (B) concentration of water, (C) applied potential and (D) concentration of NH_4F. As can be observed for the parameters; (B) concentration of water, (C) applied potential and (D) concentration of NH_4F presenting a higher level, therefore, occurs a smaller formation of nanograss on top of TiO_2 nanotubes, except for the parameter (A) chemical pretreatment which presents a lower level (no chemical treatment), which means that no pretreatment is required to avoid the nanograss formation.

The Taguchi design method was also used to identify the influences on the internal and external diameters (Table 3) of TiO_2 nanotubes (Fig. 6 and 7). In this second stage of the work, for measurable quality characteristics, the equation *larger-is-better* was used as in Eq. (2). Figs 6 and 7 show the S/N ratios calculated from Eq. (2) for different internal and external diameters of the TiO_2 nanotubes, as set out in Table 3.

This parameter (*larger-is-better*) for the internal and external diameters was chosen because, according to the literature[19,55],it is reported that TiO_2 nanotubes with larger diameter presents an better efficiency in several applications as in environmental and energy[5,12,56,57].

The values of the internal and external diameters of the samples Exp. 1 and Exp. 8 are not mentioned in Table 3 due to their irregular structure, which prevented us from estimating them (Fig. 4), but in order to execute the Taguchi method program an arbitrary value was added.

The signal-to-noise (S/N) ratio analysis is adopted to improve the statistical properties (Fig. 6 and 7). Therefore, it can be observed that the medium chemical pretreatment interferes with the internal diameter, as observed in Fig. 6. Besides, a high water concentration and the applied potential are important factors that increase the internal diameter of

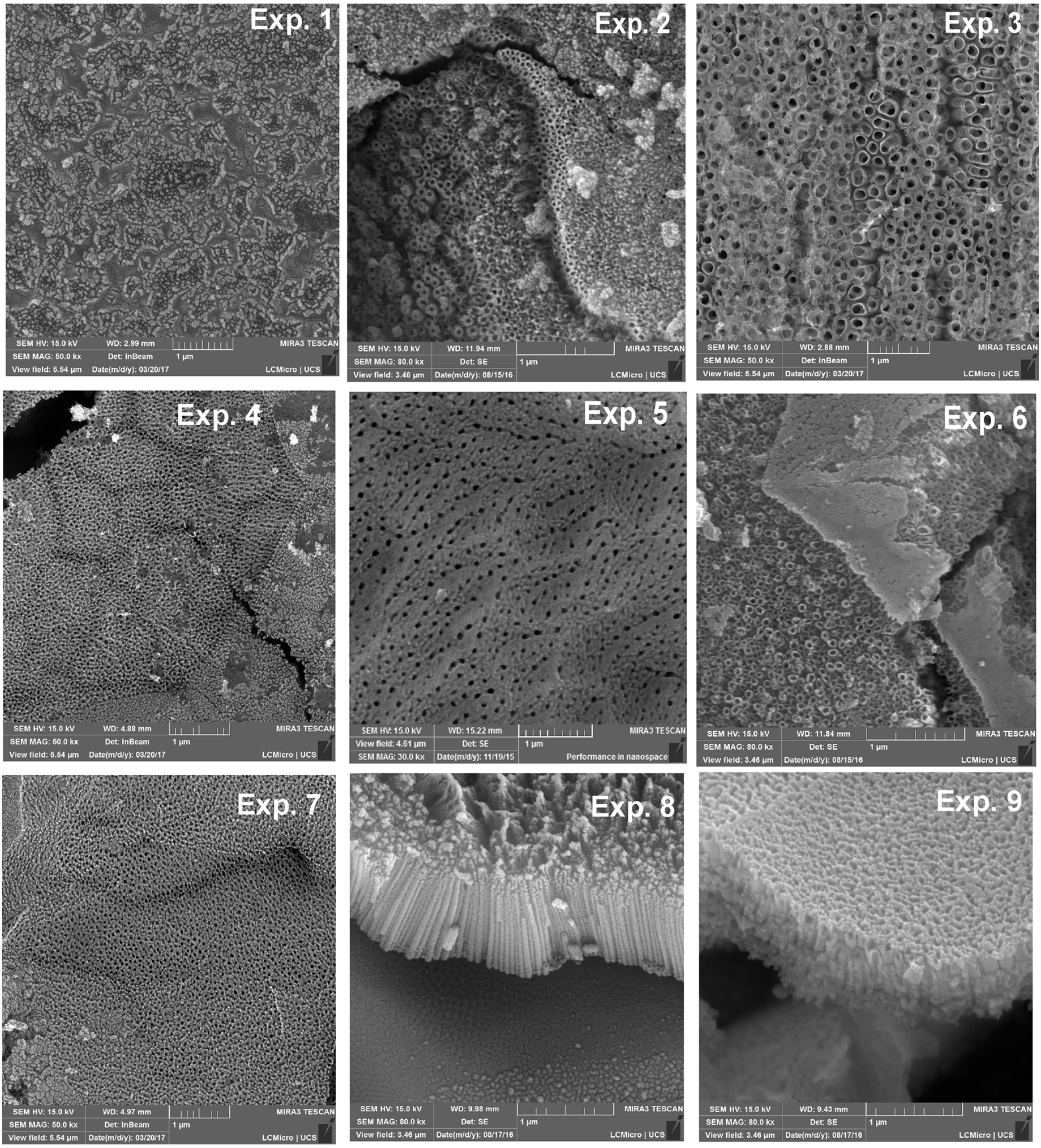

Figure 4. Top-view images obtained by FEG/SEM of TiO_2 nanotube arrays fabricated for 180 minutes of anodization and annealed at 450 °C for 3 h

the nanotubes, as the fluoride concentration at a medium level favors the increase in the internal diameter (Fig. 6).

Therefore, to obtain a larger internal diameter of the TiO_2 nanotubes, it is important to note the parameters that influence in the following order: (C) applied potential, (B) concentration of water, (D) concentration of NH_4F and (A) chemical pretreatment.

Fig. 7 shows the ranking of the factors that contribute to the increase of the external diameter in the following order (*larger-is-better*): (C) applied potential, (B) concentration of water, (A) chemical pretreatment and (D) concentration of NH_4F. In this way, nanotubes with larger external diameters are obtained.

According to the Taguchi experimental method, we show a ranking of the importance of the factors that influence the formation of the TiO_2 nanotube morphology. The parameter levels combination that simultaneously satisfy the various aspects considered (length of the nanotubes, nanograss,

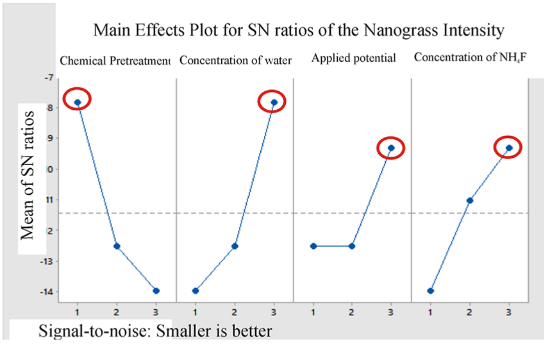

Figure 5. The trend diagram of each parameter on the mean for the nanograss (signal-to-noise (S/N) ratio)

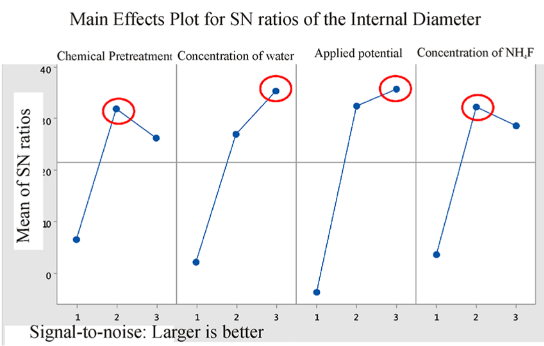

Figure 6. The trend diagram of each parameter on the mean of the internal diameter of the nanotubes (signalto-noise (S/N) ratio)

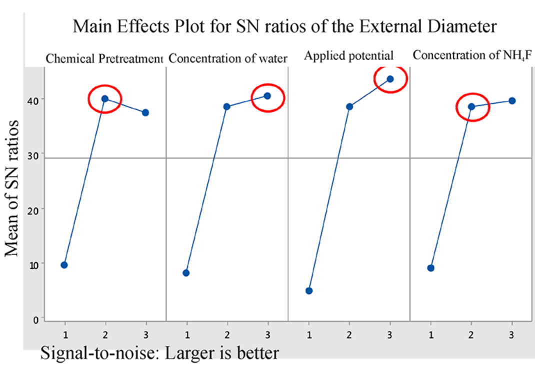

Figure 7. The trend diagram of each parameters on the mean on the external diameter of the nanotubes (signal-to-noise (S/N) ratio)

internal and external diameter of the nanotubes) in obtaining the TiO_2 nanotube morphology described in the literature[3,47,58], for the photocatalysis application, correspond the parameters used to obtain the sample Exp. 3.

4. Conclusions

- In this paper, the synthesis of TiO_2 nanotubes via the anodization method has been investigated by a Taguchi method experiment. Applied potential, chemical pretreatment, water concentration and the fluoride content were considered as the main factors that influence the anodization process. The results are summarized as follows:The results obtained from Taguchi's test design (*smaller-is-better)* show that it is preferable to obtain nanotubes with less thickness. Thus, it is necessary to observe the following order: applied potential, concentration of water, concentration of NH_4F and chemical pretreatment. Therefore, to avoid the formation of nanograss at the top of the TiO_2 nanotubes, the following order must be followed (from more to less important) when the aim is obtain nanotubes free of nanograss: chemical pretreatment, concentration of water, applied potential and concentration of NH_4F.
- Also the Taguchi method was used to identify the influences on the internal and external diameters of TiO_2 nanotubes with the parameter *larger-is-better*. Therefore, to obtain a larger internal diameter of the TiO_2 nanotubes, it is important to note the parameters that influence in the following order: applied potential, concentration of water, concentration of NH_4F and chemical pretreatment. To increase the external diameter, it is important to note the parameters that influence in the following order: applied potential, concentration of water, chemical pretreatment and concentration of NH_4F.
- The morphological analyses (Fig. 4) have shown that the sample Exp. 3 resulted in the smallest amount of surface nanograss, i.e., this condition makes it possible to obtain open top nanotubes, obtained from Ti foil without chemical pretreatment and high levels of water, potential and concentration of NH_4F, as represented in Fig. 5.

Therefore, according to the Taguchi experimental method, exhibited a ranking of the importance of the factors that influence the morphology of TiO_2 nanotubes. Thus, concludes a combination for photocatalysis applications, according to the ranking; applied potential (level 3); concentration of water (level 3); concentration of NH_4F (level 2) and chemical pretreatment (level 1).

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