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Design of Experiments (DOE) for Synthesis of Nanotubular Structured Electrodes

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Vertically nanotubular layered TiO_2 based electrodes were obtained by electrochemical anodization of Ti foils in ammonium fluoride organic electrolytes. The effect of the anodization bath composition on their photo-electrocatalytic performance was investigated. The organic solvent (S), the fluoride concentration (F) and the water content (W) in the bath were selected as influent parameters, which were varied at two levels in a set of experiments organized by means of the design of experiments technique (DOE). Aspect ratio of the nanotubes, photocurrent measured both at UV and near visible light were adopted as objective functions in order to evaluate the performances of the samples. Single and combined effects of the parameters on the objective functions have been measured.
The results indicate that the water content has no effect on the aspect ratio of the samples; however its content in the organic solvent plays a crucial role in the photocatalytic performances.

1. Introduction

In recent years, the use of TiO_2 nanometric structures has attracted considerable interest for applications in several fields of photo-electrocatalysis such as photoelectrochemical (PEC) water-splitting for generating hydrogen via the efficient utilization of solar energy (Kitano et al., 2008). As is well known, TiO_2 is the most widely used photocatalyst due to its low cost, environmental compatibility, high activity and large stability, (Fujishima et al., 2008). Specifically, nanoparticulated forms of TiO_2 are considered in order to maximize the specific surface area (i.e. reaction sites) which is a key issue for materials used in most of the heterogeneous catalytic reactions. Among the various forms, one-dimensional vertically oriented titania nanotubes, have attracted increasing interest due to their highly ordered structure and the convenient control of morphology and size (Grimes, 2007; Ghicov and Schmuki, 2009). In particular, the application of TiO_2 nanotubes as photoanodes in PEC systems has been extensively studied since they (i) offer a large internal surface area, (ii) ensure good electrical transport being ordered and strongly interconnected, (iii) provide intimate contact with the electrolyte and (iv) offer long electron lifetime (e.g. by lowering the charge carrier recombination).
Titania nanotubes can be produced by a variety of methods (e.g. sol-gel synthesis, electrodeposition, and hydrothermal processes) but the anodization of titanium foils in fluoride-based baths is one of the most widely investigated technique because it represents a very simple and useful way to obtain nanotube arrays the dimensions of which can be precisely controlled. In addition, directly back contacted electrodes can be obtained sinceTiO_2 nanotubular layers grow directly on the Ti substrate. However, the formation of TiO_2 nanotubes by anodic oxidation strongly depends on the operating conditions employed during the anodization process (Mor et al., 2006; Macak et al., 2007; Ranney et al., 2010). Applied potential, anodization time, electrolyte composition (e.g. pH, fluoride concentration, presence of organic electrolytes) and annealing temperature are some of the typical parameters that must be tailored in order to control both nanotube morphology (i.e. length and/ or the thickness) and also their crystalline structure.

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In this context, this work focuses on the effect of the anodization bath composition (i.e. organic solvent and water content and fluoride concentration) on both the structure and photo-electrocatalytic performance of TiO_2 nanotubes in the PEC water splitting reaction. For this purpose the design of experiment (DOE) technique (Box et al., 1978) has been adopted with the aim of identifying the minimum number of experiments required to evaluate both single and combined effects of the investigated parameters.

2. Experimental procedures

2.1 Synthesis of the TiO_2 samples

Each sample obtained from Ti foils (0.25 mm thick, 99.7 % metal basis, Aldrich) was previously polished by using different solutions (isopropanol, acetone and methanol) following the procedure indicated previously (Palmas et al., 2011). Then, the samples were submitted to an oxidative process in which the formation and growth of TiO_2 NT structure was performed. The anodization process was carried out in water/organic solution which always contained a certain amount of fluoride ions as pitting agent. The anodization was carried out using a conventional two electrode system in which the Ti foil was used as anode and a Pt grid as cathode at room temperature. A potential ramp was applied from open-circuit voltage (OCV) to a fixed potential (20 V) with a scan rate of 100 mV s^{-1}; then, the applied potential was maintained at this fixed value for 3 h. A final annealing treatment was required in order to transform the amorphous structure into crystalline one. Thermal treatment was performed in air atmosphere at 400°C for 1 h.

2.2 Experimental Methods

The electrochemical and photoelectrochemical performance, as well as the characterization of all the samples, were evaluated using the TiO_2 synthesized samples as working electrode (WE) in a three electrode cell. The WE active area analyzed in the tests was 1 cm^2. A platinum grid was used as counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode. The supporting electrolyte was 0.1 M KOH solution for all the tests. Photocurrents at the samples were tested under a light flux provided by a 300W Xe lamp (Lot Oriel) equipped with an IR water-filter. Suitable optical filters were used in order to select different wave lengths of the incident light. Also specific runs were performed in order to simulate the solar radiation, in which no filter (white light) was used. The photocurrent was calculated by subtracting the stable values measured in the dark from those obtained under irradiation.
Film morphology of the assembled electrodes was characterized by means of scanning electron microscopy (Zeiss Supra 40 FEG-SEM).

3. Results and Discussion

The DOE technique was used to plan the set of the experiments in which the organic solvent (S), water content (W) and fluoride concentration (F) were considered as influent parameters, and they were varied on two levels in a full factorial design. Table 1 shows the values of the coded parameters at the minimum (-1) and maximum (+1) levels. In particular, as far as the solvent was concerned, it being a non-quantitative parameter, the low and high levels were arbitrarily chosen. Low level (-1) was assigned to ethylene glycol (EG), and high level (+1) to glycerol (G). Two different ranges of water content were considered, depending on the kind of organic solvent used in the anodization solution. A range of water content around 30-40 vol% has been considered in the case of G solvent, but low levels have been used in the case of EG. According to the literature (Ye et al., 2014), the presence of high water contents in EG based electrolytes may destroy the NT structure, generating cotton-like structures on the substrate. Considering this fact, for the EG 0.5 vol% and 3 vol% of water content were used as low and high values. Two fluoride concentrations of 0.05 M and 0.1 M were considered, representing the lowest and highest levels for this factor.

Table 1: Coded parameters for the DOE analysis.

Parameter		***Fluoride concentration***	***Water content***	***Solvent***
Unit		Mol / L	vol%	-
Simbol		F	W	S
Level	-1	0.05	0.5	EG
			20	G
	1	0.1	3	EG
			30	G

For a full factorial design, in which *n* parameters are considered at *L* levels, the minimum number *N* of samples which are needed to correctly apply the DOE technique is derived as $N = L^n$. In the specific case in which 3 factors were varied at 2 levels, 8 samples were synthesized under different experimental conditions. The performance of each sample was evaluated by measuring the values of aspect ratio γ, defined by the ratio between length and diameter ($\gamma = l/\phi$) of the tubes, and the photocurrents measured at wavelengths of 365 (i_{365}) and 400 nm (i_{400}) which were adopted as objective functions in the analysis. Table 2 represents the DOE matrix which illustrates the whole plan of the experiments: the composition of the bath solution for the synthesis of the 8 samples was derived by the first three columns, in which the coded parameters were combined to indicate the specific conditions of each experiment. Y_{ij} reported in the DOE matrix indicate the response obtained at the j-th sample for the i-th objective function.

Table 2: DOE Matrix for the calculation of the experimental conditions.

Sample	Parameters			Codes for combined effects				Objective function
	F	W	S	FW	FS	WS	FWS	Y_i
1	1	1	1	1	1	1	1	y_{i1}
2	-1	1	1	-1	-1	1	-1	y_{i2}
3	1	-1	1	-1	1	-1	-1	y_{i3}
4	-1	-1	1	1	-1	-1	1	y_{i4}
5	1	1	-1	1	-1	-1	-1	y_{i5}
6	-1	1	-1	-1	1	-1	1	y_{i6}
7	1	-1	-1	-1	-1	1	1	y_{i7}
8	-1	-1	-1	1	1	1	-1	y_{i8}

As indicated by the technique, the influence of the p-th parameter (effect E_p) on the objective function Y may be evaluated by the following equation:

$$E_p = \bar{y}^{(+)} - \bar{y}^{(-)} = \frac{\sum_p y_p^{(+)} - \sum_p y_p^{(-)}}{4} \quad (1)$$

where $\bar{y}^{(+)}$ and $\bar{y}^{(-)}$ represent the mean of the values of the responses obtained from runs in which the p-th parameter was set at the highest (+1) and lowest (-1) levels, respectively. In order to evaluate the combined effects between two parameters p and q, Eq. 1 can be still used if the related columns (pq) in Table 2 are considered to identify the maximum and the minimum levels of the combination of parameters. The related responses obtained in the planned experiments are schematically represented in Figure 1. A typical cube representation is adopted where the dimension of dots in the corners indicates the relative magnitude of the related objective function values.

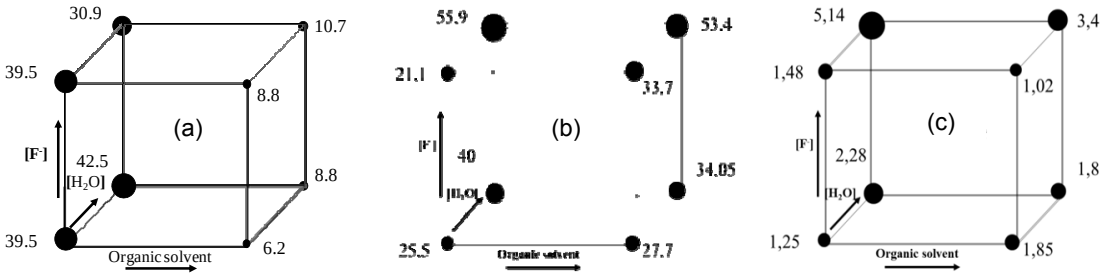

Figure 1: Cube representation of the objective functions values for all the synthesized samples: nanotube aspect ratio (a), normalised photocurrent at λ=365nm (b) and (c) at λ=400nm (values in mA/W).

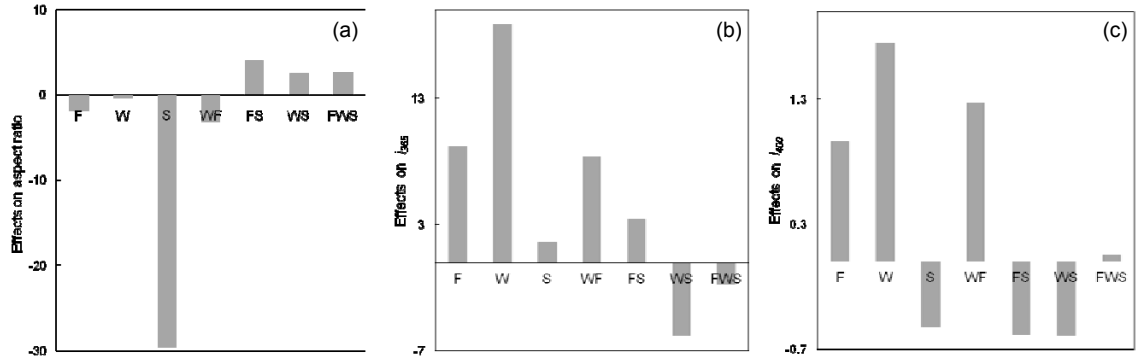

Figure 2: Effects of the parameters and their interactions on the aspect ratio (a) and on the photocurrent responses at λ=365 nm (b) and (c) at λ=400 nm. (F: fluoride concentration; W: water content; S: solvent).

Figure 2 depicts the effects calculated by equation 1. As can be observed, W content and F concentration in the anodization bath appear not to influence the morphology, while the most influential parameter on the nanotubes aspect ratio is the solvent. Accordingly, SEM analysis (Figure 3) showed longer tubes with narrow diameters for samples anodized in EG rather than in G. Also the combined effects may be considered non-significant.

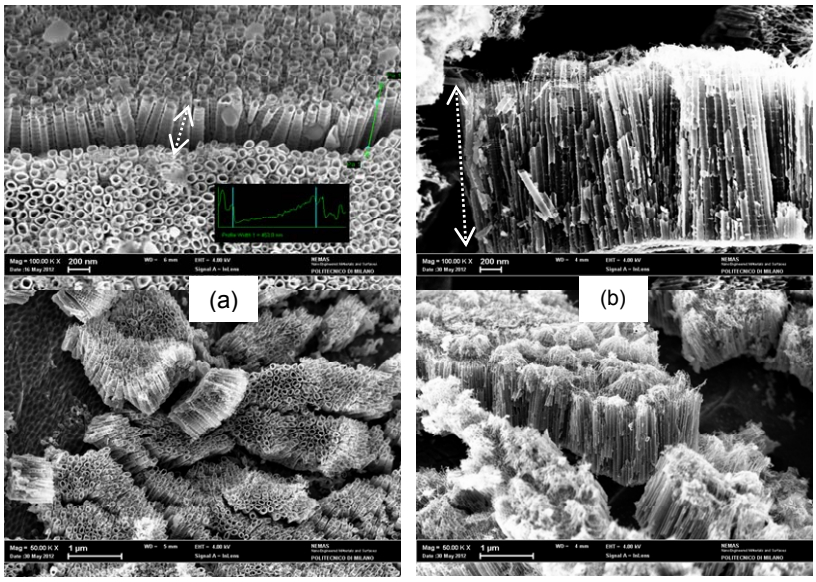

Figure 3: SEM images of the samples synthesized in G (a) and (b) in EG.

Concerning the photocurrents, for both the cases the triple effects are negligible and the most relevant single effect is that of water. Moreover, combined binary effects seem to be effective for these objective functions. In order to quantify the related importance of these effects, the half-normal probability plot has been considered, in which all the ordered (largest to smallest) absolute values of the estimated effects for the main factors are reported. As an example, Figure 4 shows the plot related to the i_{365} objective function. W is the most important effect, the related point being the only one displaced with respect to the linear trend. The analogous plot for the i_{400} function also indicated a relevant WF binary effect.

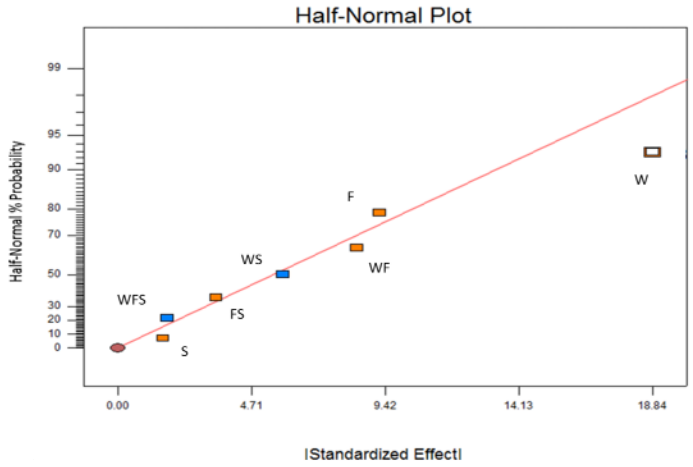

Figure 4: Half normal probability plot of effects for the i_{365} objective function.

On this basis, the study has was extended by obtaining new samples in which, other conditions being the same, the content of water in the electrolytic anodization bath was varied over a wider range as reported in Table 3. In particular an intermediate percentage of water content was selected for samples obtained in EG, whereas two values were selected externally to the previously investigated range, for those obtained in G.

Table 3: Anodization conditions for the three representative samples.

Sample	**Parameter / Unit**		
	Fluoride Concentration / M	Water content / vol%	Solvent / -
9	0.1	10	G
10	0.1	40	G
11	0.1	1	EG

The photocurrents measured at these samples under UV irradiation are reported in Figure 5 along with the previous results as a comparison. Due to the different range of water content in the two solvents, data in Figure 5a) and b) have been separately considered for G and EG, respectively. Also, photocurrents under white light were measured in order to test possible application of these samples in the visible range of light.

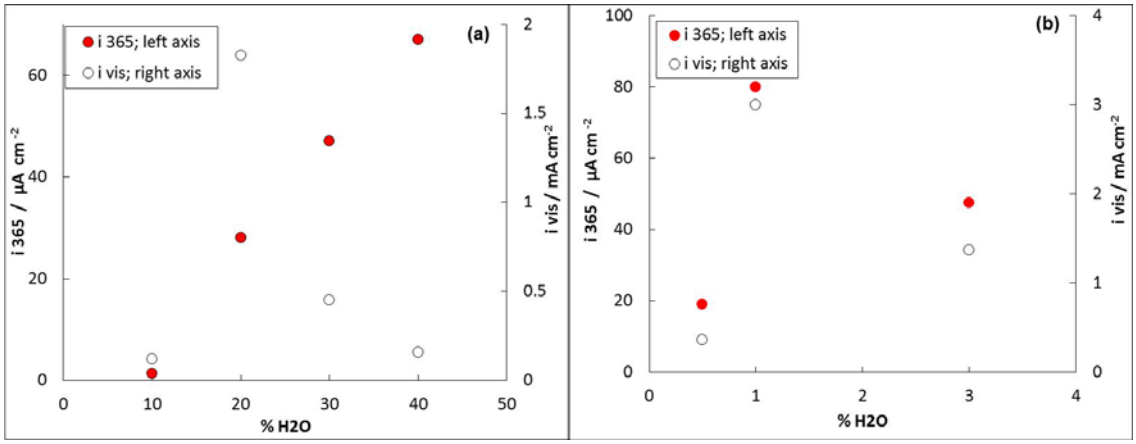

Figure 5: Photocurrent values measured at λ=365 nm and under visible light for samples synthesized in G (a) and (b) in EG solutions with different water content.

The data reported in Figure 5 may suggest that a water content of about 1 vol% could be used in the bath EG solution to obtain samples performing well under UV and visible light.
For the samples prepared in G, Figure 5a indicates that 20 % water content could be the best for samples working in the visible range. A better performance can be obtained under UV irradiation if the percentage of water is increased beyond the 40 vol%. This may suggest the use of inorganic solutions in the anodization process.

4. Conclusions

DOE analysis proved to be a useful and viable method to investigate the effects of different parameters on both the structure and the performance of nanotubular samples. The kind of solvent was the most important factor determining the aspect ratio of nanotubes, while water content was the most influential parameter on the photocurrent measured at samples in the UV range. Finally, data indicated a water content of about 1 vol% to be used in the ethylene glycol bath solution to obtain samples performing well under UV and visible light. For samples prepared in glycerol/water solution, 20 % water seems to be a good choice for visible light. The increasing trend of photocurrents obtained for samples prepared in glycerol with increasing water content, may suggest that inorganic solvents could be a better choice to obtain improved performance in the UV range.

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