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Short Communications

Effect of Surface Morphology of ZnO Electrodeposited on Photocatalytic Oxidation of Methylene Blue Dye
Part II: Estatistical Study

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In this paper, we did a statistical study to find the conditions of voltage, temperature and deposit time that allow us to control the grain number in electro-deposited ZnO thin films, since this parameter influences their photocatalytic properties. For this reason, we obtained electro-deposited ZnO thin films on indium tin oxide (ITO) coated glass substrates. The deposition conditions were established in an experimental design 2^3. Our results showed that with the right combination of variables voltage, temperature and deposition time, we can obtain the optimal grain number on ZnO thin films for the best photocatalytic efficiency.

Keywords: ZnO, grain number, factor, experimental design

1. INTRODUCTION

There are several reports of single-factor studies on the effect of the physical properties of ZnO thin films such as: crystal structure, surface area, preferred orientation, size and shape of particles in optical, electrical and photocatalytic applications [1-11], hence, it is of great importance to control the physical properties of ZnO.

The efficient control of these properties requires the study of simultaneous influence of several variables or parameters of deposit (multifactorial studies). For this reason, statistical experimental design is an indispensable tool.

Statistical experimental designs [12] are more efficient than the traditional experiment of moving a factor at once, because when there is interaction between factors, one moves away from the optimal process. In contrast, by factorial experimentation where different combinations of factor levels are tested, it is possible to find from the first designed, the operating conditions close to optimal with less experimental runs.

Some of the most important variables by cathodic electro-deposition in an aqueous environment are: temperature, applied potential, deposit time, chemical composition of the electrolyte and the substrate type [13-17].

In this paper we analyze statistically the effect of the combination of these variables on the aspect of grain size of ZnO electro-deposits and thus obtain sufficient information to get the optimal grain number and reach the greatest photocatalytic degradation. This study includes an experimental design 2^3 (2 levels and 3 variables), as shown in Table 1.

Table 1. Experimental Design

Coded parameters	Study Parameters	Low level (-)	High level (+)
A	Electrodeposition Voltage	-900 mV	-850 mV
B	Electrodeposition temperature	60 ^{0}C	70 ^{0}C
C	Electrodeposition time	5 min	10 min

2. EXPERIMENTAL

The electro-deposits were carried out using a bipotenciostat "Pine Instruments" and the methodology for the growth of ZnO was reported in Part 1 of this article.

3. RESULTS AND DISCUSSION

Table 2 shows the labels of ZnO samples obtained for each combination of variables of the electro-deposits and the grain number for each sample.

Table 2. Labels of the samples according to the levels of the main parameters used and the results of grain number obtained by SEM.

ID of samples	A (V)	B (^{0}C)	C (min)	grain number
M1	-	-	-	55
M2	+	-	-	65
M3	-	+	-	37
M4	+	+	-	60
M5	-	-	+	28
M6	+	-	+	33
M7	-	+	+	40
M8	+	+	+	22

3.1 Statistical analysis for response variable (grain number)

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Estimated effects for Grain number
--------------------------------------------------
average                            = 42.5  +/- 4.5
A:Electrodeposition voltage        = 5.0   +/- 9.0
B:Electrodeposition temperature    = -5.5  +/- 9.0
C:Electrodeposition time           = -23.5 +/- 9.0
AB                                 = -2.5  +/- 9.0
AC                                 = -11.5 +/- 9.0
BC                                 = 6.0   +/- 9.0
--------------------------------------------------
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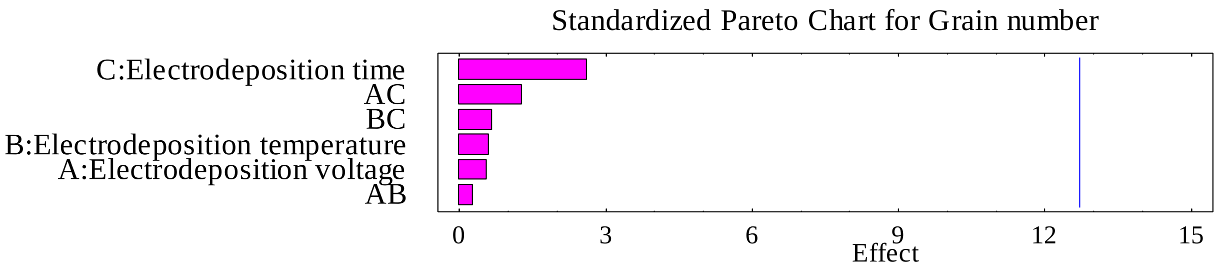
a)



b)

Figure 1. a) Estimated effects and b) Standardized Pareto chart for the response variable (grain number) of the experimental design

The calculation of the effects of the factors for grain number (Figure 1a) for each electrodeposited sample was performed using STATGRAPHICS Plus, Version 4.1. The effects are plotted in a Standardized Pareto chart (Figure 1b) because it is easy to decide if the effect affects the response variable to a confidence level of 95%, so if the bar representing an effect is greater than the critical value represented by the vertical line, then the effect is statistically different from zero and affect the response.

The preliminary interpretation of Standardized Pareto chart indicates no factor affecting the response variable to a significance level of 95%. To corroborate this, statistical study was carried out by an analysis of variance (ANOVA) at a 95 % confidence level, the assumptions for ANOVA were the following:

null hypothesis H_0: effects $A=B=C=0$
alternative hypothesis H_A: effects A, B, C $\neq 0$

and

null hypothesis H_0: effects $AB=AC=BC=0$
alternative hypothesis H_A: effects AB, AC, BC $\neq 0$

These hypotheses are tested by ANOVA (Table 3), if an effect has a p-value less than 0.05, then we accept the alternative hypothesis and this effect influences on the response. In addition, the smaller the p-value, the more significant is this effect.

Table 3. Analysis of variance for grain number

Source	Sum of squares	Df	Mean Square	F-Ratio	P-value
A:voltaje	50.0	1	50.0	0.31	0.6772
B:temperature	60.5	1	60.5	0.37	0.6508
C:time deposit	1104.5	1	1104.5	6.82	0.2328
AB	12.5	1	12.5	0.08	0.8275
AC	264.5	1	264.5	1.63	0.4227
BC	72.0	1	72.0	0.44	0.6257
Total error	162.0	1	162.0		
Total (corr.)	1726.0	7			
R-squared = 90.6141 percent					
R-squared (adjusted for d.f.) = 34.299 percent					

The preliminary interpretation of the results indicates that there is no factor that affects the response to a significance level of 95%. To clarify what factors really influence on the response variable, only significant effects are included in the Standardized Pareto chart (Figure 2) and in the final ANOVA (Table 4). Effects A, B, AB and BC have little influence on the response variable because have a high value of p and practically does not contribute to the value of adjusted R^2, hence, were not considered.

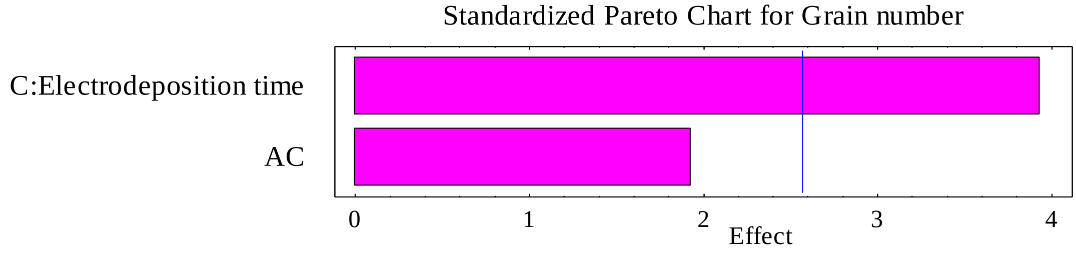


Figure 2. Standardized Pareto chart for grain number showing only significant effects

Table 4. Improved analysis of variance for number of grains

Source	Sum of squares	Df	Mean Square	F-Ratio	P-value
C:time deposit	1104.5	1	1104.4	15.47	0.0110
AC	264.5	1	264.5	3.70	0.1123
Total error	357.0	5	71.4		
Total (corr.)	1726.0	7			
R-squared = 79.3163 percent					
R-squared (adjusted for d.f.) = 71.0429 percent					

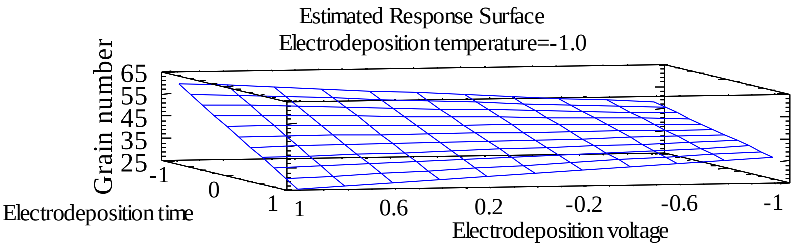
The standardized Pareto diagram and the ANOVA clearly show that statistically the effect C influences the response variable to a confidence level of 95%, however, we trust that the CA effect also influences the response, because it contributes to adjusted R^2 approximately with 13 percent and the bar representing the effect is near the critical value.

The adjusted model of the response variable in the experimental region was obtained by the important factors and is:

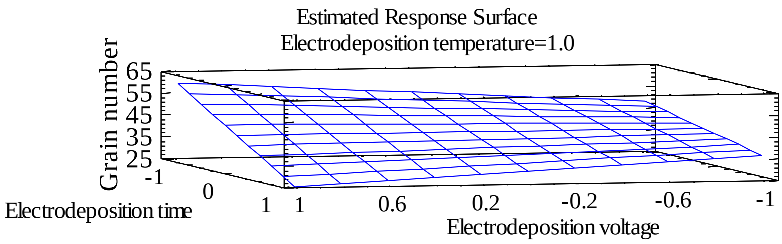
Grain number = 42.5 – 11.75 * Electrodeposition time – 5.75 * Electrodeposition voltage * Electrodeposition time

Since interactions have priority over the effects, then we interpret the interaction AC through its response surface. The response surface is a visualization of the fitted model in the experimental region. Figure 3a and 3b show the response surface graphs of the factors A and C for temperatures of 60 and 70 ^{0}C, the general trend is the increasing grain number with the decrease in deposit time and voltage rise.

This may be due to the fact that a more negative voltage causes increase production of hydrogen, something similar was observed for Tinting et al [17], this could limit the number of growth nuclei and hence decrease the grain number. On the other hand, more time of deposit implies larger grain size and a coalition between adjacent grains and hence a decrease in the grain number, something similar was observed for Jaeyoung Lee [18].



a)



b)

Figure 3. Estimated response surface that comes from the graph of the factors A and C for grain number a) for electro-deposition temperature of 60 ^{0}C and b) for electro-deposition temperature of 70 ^{0}C

As shown, we can choose the values of time and voltage of electrodeposition to reach the optimal grain number for maximum photocatalytic degradation, as shown in Part 1of this paper.

4. CONCLUSIONS

The statistical analysis supplied valuable information to decide on what factors work to find the optimal morphology for photocatalysis. Also, it was showed that by an appropriate combination of growth parameters, we can control the grain number on ZnO electro-deposits and maximize the degradation of methylene blue.

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