Experimental statistic design applied for obtaining Zn:xCe by microwave-assisted hydrothermal method with photocatalytic property

Y. F. GOMES*, A. K. FREITAS, R. M. NASCIMENTO, M. R. D. BOMIO, C. A. PASKOCIMAS, F. V. MOTTA

Departamento de Engenharia de Materiais, Universidade Federal do Rio Grande do Norte, 59078-900, Natal/RN, Av. Sen. Salgado Filho, 3000, CEP 59072-970, Brazil

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Abstract: In this study, the nanostructures of pure ZnO and ZnO:Ce³⁺ were prepared using statistic design—factorial design 3³⁻¹—3-level and mixed-level factorials and fractional with replicates in the central point, totaling 11 experiments. The experiments were performed using the microwave-assisted hydrothermal (MAH) method with Ce³⁺ concentration of 2 and 4 mol% at 60, 110, and 160 °C for 10, 20, and 30 min. X-ray diffraction (XRD), scanning electron microscopy (SEM), and optical diffuse reflectance were used to characterize the products. The fractional factorial design indicated the optimal design area, and the studies were continued by ridge analysis. The analysis of variance (ANOVA), the Pareto, and the model adjusted to the conditions proposed in this study due to the determination coefficient of 99.9%, variance (R²), and response surface generated were satisfactory, thus having an optimization in the process of obtaining ZnO doped with Ce.

Keywords: hydrothermal; ZnO; cerium; photocatalytic activity; factorial design 3³⁻¹

1 Introduction

Doping ZnO nanostructures is of great interest for a variety of practical applications, especially doping with rare earth elements [1]. In recent, the nanostructures doped with rare earth elements such as Ce, Y, and I are getting a lot of attention due to their optical properties. Particularly, Ce having a unique optical characteristic may be an ideal material for high power laser, light diode, etc. [2,3].

Zinc oxide is an intrinsic n-type semiconductor with band gap \(E_g = 3.37\) eV and large binding energy 60 meV, which crystallizes in the hexagonal system with wurtzite type [4,5]. Because of the high photocatalytic activity, low cost, and present ecological aspects [6,7], ZnO has been widely used as photocatalyst [8].

To date, several routes for the preparation of ZnO nanostructures doped with rare earth elements have been reported, including hydrothermal method, magnetron sputter deposition, pulsed laser deposition, photolithography, and wet chemical etching. However, microwave-assisted hydrothermal (MAH) method is more advantageous because of its easy operation, low cost, lower temperature, and greater control of morphology [9]. This is the method used in this study along with the statistical design in order to optimize the process of synthesis. Statistical design of experiments has been increasingly employed by engineers and researchers for screening out main effects and

* Corresponding author.
E-mail: yfeliciano@gmail.com
optimization matters. The ease of obtaining data over a wide range experimental region with a fair degree of accuracy makes it very attractive. This approach helps to better understand how the change in a group of parameters affects the response. For this study, we used a factorial design with 3-level and mixed-level factorials and fractional. These designs are a generalization of the $2^k$ designs, assuming in the $3^k$ designs that the factors are all quantitative. Most $3^k$ designs are only useful where the factors are quantitative. With $3^k$ designs, we are moving from screening factors to analyzing them to understand what their actual response function looks like. A combination of the levels of the parameters, which leads to certain optimum response, can also be located through this approach. The factorial design can cover the main and interactive effects of the parameters within the whole range of selected parameters [10–13].

Fractional factorial design is a reliable method to simplify the process of identifying the most influential preparation variables. This approach reduces the number of experiments required to identify the variables in a statistically significant manner [14].

Fractional factorial design was used to optimize the synthesis process of Zn$_{1-x}$Ce$_x$O to determine a means to save time, thus reducing the number of experiments for analyzing the input variables that would influence the process.

This study used a factorial planning of variables in the process of obtaining degradation photocatalysis at different levels of doping, temperature, and time along with the process of synthesis by MAH, totaling three input variables ($k=3$) for the synthesis process. The design of experiments (DOE) approach can be used. Within the scope of DOE, factorial design and response surface methodology are important tools to determine the effects of process parameters and their interactions, as well as to optimize the process conditions [15–19].

2 Experimental

2.1 Materials and methods

Using the MAH method, ZnO:xCe$^{3+}$ powders were obtained. For this synthesis, zinc nitrate (Zn(NO$_3$)$_2$) and cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O) as dopant were dissolved in 80 mL deionized water under constant stirring. The cerium ions were added in the following percentages: 0, 2, and 4 mol%. The pH of the solution was adjusted to 10 by adding NH$_4$OH, and the mixture was then transferred to a Teflon autoclave. The system was sealed and placed into a domestic microwave oven (2.45 GHz, maximum power 800 W). The system consisted of: (a) drilling of a 3 mm diameter opening in the upper part of the oven cavity for the passage of a thermocouple, (b) magnetron control by an external temperature controller, and (c) addition of the microwave cell (apparatus developed for this purpose) within the cavity of the oven. The thermocouple was connected to an external controller, which received the information of oven temperature from the thermocouple and controlled the activity of the oven magnetron. The reaction system was heat treated at 60, 110, and 160 °C for 10, 20, and 30 min (heating rate 25 °C/min) according to the statistical design used.

The autoclave was cooled to room temperature naturally. A white product was separated by centrifugation, washed with deionized water and ethanol, and dried at 60 °C in air.

2.2 Photocatalysis experiments

The photocatalytic degradation experiment was performed in a box containing a glass with lamps mounted horizontally, this being the source of radiation. Before going to degradation box, 0.05 g of powders was added in a 50 mL solution of methylene blue and was kept stirred for 15 min on a magnetic stirrer; thereafter, the same solution was maintained under stirring in an ultrasound for the same period of time. Samples were withdrawn at intervals of 30 min and then centrifuged before analysis. To measure how much of methylene blue was degraded, UV–Vis spectrophotometer was used, which analyzed maximum absorption (MA) level at 664 nm, corresponding to its wavelength of maximum absorption; these percentages of material degradation efficiency were utilized as response surface according to the statistical design study.

2.3 Experimental design and characterization of the material

The fractional factorial design used increases the amount of information obtained and reduces the number of experiments. To determine the influence of these parameters on the MAH synthesis, one of the methods of response surface methodology (RSM) was used as an effective tool to get an insight about the influential parameters affecting the degradation and also to
optimize the operating conditions [13]. RSM is a combination of mathematical and statistical techniques, which is an effective tool for developing, improving, and optimizing different processes. This design study has analyzed the synthesis of ZnO:CeCe by MAH with the conditions of doping, temperature, and time in the degradation. The critical ranges of the factors were selected based on a set of preliminary experiments. Montgomery described an experiment conducted in order to identify the factors that contribute to the degradation. Three factors were considered: doping, temperature, and time at three different levels. The wavelengths related to higher absorbance peak of the degradation of Zn1−xCe2O obtained by analysis of the UV–Vis spectroscopy were the response variables with the percentage of doping efficiency values [11–14,20].

Data from 3-level and mixed-level factorials and fractional were subjected to the following quadratic equation model to predict the system response and estimate the coefficients by the least-squares regression, as shown in Eq. (1):

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<j}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_i x_i^2 + \epsilon \]  

where \( Y \), \( \beta_0 \), \( \beta_i \), \( \beta_{ij} \), and \( \beta_i \) are the predicted response, the constant coefficient (intercept term), the linear coefficient, the quadratic coefficient, and the interaction coefficient, respectively. The parameters \( x_i \) and \( x_j \) are independent variables; \( k \) and \( \epsilon \) are the number of factors and the residual term allowing uncertainties between observed and predicted values, respectively. STATISTICA 7.0 software was used for the regression analysis to estimate the coefficients of the response function. The statistical significance of the model equation was analyzed by the analysis of variance (ANOVA). Three-dimensional (3D) surface and two-dimensional (2D) contour plots were developed while holding a variable constant in the quadratic model. The experimental and predicted values were compared to validate the model. The values of polynomial coefficients and the response surface of the second-order model were obtained using STATISTICA 7.0 software, and the model was validated for the process conditions used in this study.

The response function (regression model) developed and the response surface placed over the region around the current selected conditions could be used to predict the response result of any adjustment of independent factors. The characterization of the material was determined by X-ray diffraction (XRD) using model Rigaku with radiation tube with Cu ka. The calculations to determine the crystallite size were run through the diffraction peaks to the ZnO plane, represented by Scherrer’s equation as shown in Eq. (2):

\[ t = \frac{K\lambda}{\beta \cos \theta} \]  

where \( t \) is the mean size of the ordered (crystalline) domains, \( K \) is the typical value of about 0.9, \( \lambda \) is the X-ray wavelength, \( \beta \) is the line broadening of full width at half maximum (FWHM), and \( \theta \) is the Bragg angle.

### 3 Results and discussion

The identification of significant factors was performed by fractional factorial design with replicates at the central point, with preliminary UV–Vis spectroscopy results corresponding to peaks of rudiment of the efficiency in this synthesis process of Zn1−xCe2O powders as response surface shown in Table 1.

The experimental results shown in Table 2 were analyzed using the STATISTICA 7.0 software and analysis of variance (ANOVA), as the ANOVA would show the comparison between the means developed in this study, which evaluates if the effect and interaction between the investigated factors are of significance with regard to the experimental error; the higher the \( F \) value is, the greater the difference among the studied factors.

Table 1  Levels and values of the operating parameters

| Operating factor | Level -1 | Level 0 | Level +1 |
|------------------|----------|---------|----------|
| Doping (mol%)    | 0        | 2       | 4        |
| Temperature (℃)  | 60       | 110     | 160      |
| Time (min)       | 10       | 20      | 30       |

Table 2  Design matrix of fractional factorial design with real, coded values and the results

| Run No. | Code | Doping level | Temperature level | Time level | Efficiency of degradation (%) |
|---------|------|--------------|-------------------|------------|-------------------------------|
| 1       | A    | -1           | -1                | -1         | 0                             |
| 2       | B    | -1           | 0                 | 1          | 13.79                         |
| 3       | C    | -1           | 1                 | 0          | 12.13                         |
| 4       | D    | 0            | -1                | 1          | 0                             |
| 5       | E    | 0            | 0                 | 0          | 25.56                         |
| 6       | F    | 0            | 1                 | -1         | 12.26                         |
| 7       | G    | 1            | -1                | 0          | 0                             |
| 8       | H    | 1            | 0                 | -1         | 25.56                         |
| 9       | I    | 1            | 1                 | 1          | 16.63                         |
| 10      | J    | 0            | 0                 | 0          | 25.49                         |
| 11      | K    | 0            | 0                 | 0          | 25.50                         |
parameters is. The significance of the main factors and their interactions were evaluated by the F-test with confidence level of 95% and Pareto method [10,11].

The results of the ANOVA analysis are presented in Table 3, showing that all the effects and interactions between factors are significant (p < 0.05); this shows that the study presented a real difference among the studied parameters and proved that it is not something that happened by chance. The value of p < 0.05 means that there is just 5% of chance of this analysis to be a result of occasionality, which gives reliability to the test running with the studied factors that are covered in this work [13,14].

Estimated effects and coefficients are listed in Table 4. The experimental error and the main factors and their interactions were evaluated by the F-test with a confidence level of 95%; this reliability shows that the analyzed results have a real sample of statistical significance and could be executed in a satisfactory way to the related cases and parameters discussed in this work [11].

XRD was used to verify the crystal structure and purity of the samples. Figure 1 presents the X-ray diffractograms of Zn$_{1-x}$Ce$_x$O powders as response surface obtained according to the experimental plan, showing its crystallization with the presence of phase that identifies the formation of zinc oxide having the wurtzite type hexagonal structure. This was verified by standard XRD crystallographic record with the JCPDS No. 36-1451 through the search-match program, which indicated the incorporation of cerium ions in zinc oxide network. Through observing the formation of a single phase crystal structure for pure ZnO and ZnO with increasing cerium ions, 2 and 4 mol%, there is formation of a secondary phase corresponding to cerium oxide (CeO$_2$). By the MAH treatment with the studied temperatures according to the statistical design, the formation of additional phase was observed [21].

In the XRD patterns, we can see that the statistical design with 11 experiments and replicates at the central point, at temperatures of 60, 110, and 160 °C for the time of 10, 20, and 30 min; temperature of 60 °C does not get stage for ZnO nor for ZnO doped with cerium; therefore these values are not used in this study. It is observed that all samples have Müller index compatible with the formation of the wurtzite phase with unit cell in the compact hexagonal system and the formation of the secondary phase in the samples doped with 2–4 mol% of cerium ions. The reduction in the intensity of the diffraction peaks when comparing pure ZnO and ZnO doped with rare earths is due to the ionic radii of Nd$^{3+}$ (0.098 nm), Eu$^{3+}$ (0.095 nm), and Ce$^{4+}$ (0.087 nm) being larger than that of Zn$^{2+}$ (0.074 nm), causing the expansion of the network [13,22,23].

According to Eq. (2), the measurement was Scherrer crystallite size using Unit Cell program, obtaining the values of network parameters ($a$ and $c$) and unit cell volume. These values are shown in Table 5, to temperatures of 110 and 160 °C. The data given in Table 5 are compared with theoretical actual values by JCPDS No. 36-1451 where $a = 3.25$ Å, $c = 5.20$ Å. These values compared to the theoretical values show that the

| Table 3 ANOVA for the suggested model |
|--------------------------------------|
| Source | DF | SS | MS | $F$ | $p$ |
| (1) Doping | 1 | 44.118 | 44.118 | 5.86051 | 0.094097 |
| (2) Temperature | 1 | 280.440 | 280.440 | 37.25216 | 0.008837 |
| (3) Time | 1 | 9.127 | 9.127 | 1.21234 | 0.538252 |
| (1) Doping × (2) temperature | 1 | 27.550 | 27.550 | 3.65965 | 0.151675 |
| Pure error | 3 | 22.584 | 7.5282 |
| Total | 10 | 1132.248 |

DF: degree of freedom; SS: sum of square; MS: mean square; $F$: F-test.

| Table 4 Estimated effects and coefficients for the suggested fractional factorial design |
|--------------------------------------|
| Factor | Effect | Standard error | (3) Time | $p$ | -95% confidence limit | +95% confidence limit |
| Mean/interaction | 11.76519 | 0.880058 | 13.36865 | 0.009065 | 8.96445 | 14.56592 |
| (1) Doping | 5.42333 | 2.240261 | 2.24026 | 0.094097 | 1.70618 | 12.55284 |
| (2) Temperature | 13.67333 | 2.240261 | 2.46667 | 0.094097 | 2.72377 | 4.66284 |
| (3) Time | 4.60111 | 2.30165 | 5.42333 | 0.094097 | 1.70618 | 12.55284 |
| (1) Doping × (2) temperature | 4.54620 | 1.790653 | 2.46667 | 0.094097 | 1.70618 | 12.55284 |
variation in the size of unit cell is small.

The scanning electron microscopy (SEM) analysis (Fig. 2) shows that the samples of pure ZnO have large amounts of ZnO with similar nanoparticles. Among the particles of ZnO doped with 2 mol% cerium at the same time, 110 °C temperature provides a better defined flower shape, and 160 °C temperature keeps very similar shape to that morphology of pure ZnO, but a greater amount of clusters and larger particle size. The particles of ZnO doped with 4 mol% cerium, at temperature and time of 110 °C, 10 min and 160 °C, 30 min, show the morphology of these particles. Besides different temperature, time for these samples is different, so the sample taking less time, which is 110 °C for 10 min shows a greater amount of clusters, while 160 °C for 30 min shows clusters and the formation of the flower type morphology.

Figure 3(a) represents the photocatalytic activity of the ZnO samples doped with 2 and 4 mol% cerium at 110 °C for 20 min, and Fig. 3(b) represents the photocatalytic activity of the ZnO samples doped with 2 and 4 mol% cerium at 160 °C for 20 min. The difference between the materials used is temperature, where the best results have been obtained from increasing temperature.

The increased photocatalytic activity of doped ZnO nanostructures can be attributed to decreased holes. However, these ions can act as a center of recombination between the photo excited electron and hole during the photocatalysis processes [24].

The doping of ZnO with Ce is expected to increase the amount of surface defects, also refers to the creation of centers of traps which increase the photocatalytic efficiency [21]. The cerium ions can also act as effective “traps” to trap the conduction band electrons, eliminating or reducing the possibility of recombination. This may cause the transferring of electrons created by the redox reaction for generating free radicals ·OH which cause the degradation of the dye [25]. Oxygen vacancies in the catalytic surface can also serve as traps for the conduction band electrons. But the high concentration of Ce causes decrease in the number of free electrons due to the imprisonment of these ions within Ce, reducing photobleaching [26].

Through the reflectance of the materials, it is possible to measure the energy band gap of the materials. These values are shown in Table 6.
Table 6  Material code and energy band gap values $E_g$

| Code | $E_g$ (eV) |
|------|-----------|
| B    | 3.22      |
| E    | 3.15      |
| H    | 2.94      |
| C    | 2.94      |
| F    | 2.96      |
| I    | 2.99      |

From the table, we can see that with the dopant, there is a reduction in the energy band gap, because the impurity or dopant causes irregularity in the crystal lattice, affecting energy levels and providing new current carriers [15]. The ZnO doped with Ce shifts the absorption edge to the visible range and reduces the range of the band gap. Therefore, that is the largest electron easily moving from the valence band to the conduction band [8, 22, 23, 27, 28].

Figure 4 shows the predicted values versus observed values using the model equation obtained from the data of the response surface of UV–Vis spectroscopy with effect of efficiency of degradation. Effects with less than 95% significance according to the $F$-test used in this study are not reported.

From the values obtained from response surface by UV–Vis spectroscopy analysis, it is possible to obtain an empirical model with first-order interaction that is able to make predictions within the study range for the five variables. The multiple regression analysis of the resulting empirical data in the process of synthesis to the following model is expressed in Eq. (3):

$$Y = 11.76 + 2.71D + 0.62D^2 + 6.83T + 7.39T^2 - 1.23t + 2.30t^2 + 3.42DT$$ (3)

The wavelength model equation is expressed for the following interval ($-1$, $0$, $+1$), i.e., variables doping, time, and temperature are valid in the range from $-1$ to $+1$. The equation with coded values is used for independent variables or interactions between variables, whereas the response variable ($Y$) is the wavelength given in degradation efficiency of the percentages. For the experimental conditions used in this study, the determination coefficient of the proposed mathematical model can explain approximately 99.9% of the variance ($R^2$).

Figure 5 illustrates the Pareto chart in which the five input variables with values greater than $p = 0.05$ at the right of the line were significant; the temperature has greater statistical significance compared to the other factors studied.

Figure 6 shows the response surfaces with the best

Fig. 5 Estimated effects and coefficients for the suggested fractional factorial design.

Fig. 6 Response surfaces and contour plots showing the effect of the independent variables’ positive correlation with the variable yield response.
conditions used in the experiments and their statistically significant interactions. As observed by ANOVA and Pareto, the best interactions are the conditions studied in this process given by the relationship between doping and temperature and doping and time.

4 Conclusions

The study of optimization along with the statistical design in order to optimize the synthesis process of ZnO doped with cerium by MAH was analyzed.

The statistical study shows effects with less than 95% significance according to the F-test; for the experimental conditions used in this study, the determination coefficient of the proposed mathematical model can explain approximately 99.9% of the variance ($R^2$). The Pareto chart in which the three input variables with values greater than $p = 0.05$ at the right of the line were significant; temperature has greater statistical significance compared to the other factors studied and followed by doping coming to be a significant statistical criteria for the study. The best interactions are the conditions studied in this process given by the relationship between the doping and temperature and doping and time.

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