Improving Dimensional Stability of Ag-doped TiO_2 Nanoparticles Through Experimental Design

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The efficiency and competitiveness of using nanomaterials can be increased through introducing scientific experimental designs. For obtaining experimental models which can better approximate the real technological systems, a sufficient number of control factors and of necessary experiment units should be taken into account, having in view their economical aspect, too. Considering the importance of Ag-doped TiO_2 nanoparticles in such domains as industry, environmental protection, health, etc., it is important for manufacturers to obtain nanoparticles of equal dimensions. The present paper is analyzing the ways of improving dimensional stability of Ag-doped TiO_2 nanoparticles produced by the microwave-hydrothermal (M-H) method. In one case, a two-level L_8 Taguchi design was used in 8 experiments, with seven control factors. In the other case, the Draper-Lin design of 40 experiments for 7 factors at two levels was utilized. It has been found out that the L_8 Taguchi experimental design offers the same results as the Draper-Lin experimental design, but with much fewer experiments.

Keywords: *TiO_2, Ag, doping, experimental design, Taguchi, draper-lin.*

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INTRODUCTION

Titanium dioxide (TiO_2) has been intensively used as a photocatalyst (see an overview and future prospects of TiO_2 photocatalysis in [9]). It also has many applications for environmental protection, such as atmospheric pollution control, sewerage treatment, etc. (See a review in [3]). Nowadays special interest is paid to elaboration of adequate techniques of synthesis, for instance, the microwave-hydrothermal (M-H) and fast hydrothermal [2], methods, to facilitate a strict control of nanoparticles dimensions. Compared with other antimicrobial agents, TiO_2 nanoparticles, used in microbiology and medicine, attracted much attention because of their adequate stability but also because they are environmentally benign, safe, cheap, nontoxical, bioactive, etc. Also TiO_2 has a great catalytic potential, serving as an active redox agent for water and air purification.

In order to be efficient, it is important that Ag-doped TiO_2 nanoparticles have certain features such as high purity and unitary chemical composition; besides, their dimensions must enroll in a uniform, narrow and controllable distribution, form and morphology.

In addition to obtaining nanocrystals by such methods as sol-gel, spray-pyrolysis, precipitation, solvothermal, electrochemical, combustion, etc., there is another method which has many advantages, namely, hydrothermal method. The main advantages of this method are as follows: due to high pressures it allows syntheses at lower temperatures than at room temperature, crystallization duration is relatively low, synthesis conditions can be easily replicated, energy consumption is low, etc. However, it has certain drawbacks, such as low crystallization speed and absence of an effective agitation of the solution to deliver germ of crystallization with fresh nutrient from the solution. Then, thermal inertia is high because heating and cooling processes take place through autoclave steel walls As the heating gradient is low some unwanted tranzitory processes may appear, such as premature crystallizations and dimensional stability of nanoparticles, which cannot be controlled rigorously. Some of those drawbacks can be eliminated by using a microwave field as the heating method. While manufacturing the autoclave permeable to microwaves (usualy electromagnetic radiation with approximately 2.45 GHz) from materials like Pyrex glass or quartz, conductive solvents from solution will absorb energy and therefore will be quickly heated from inside. Moreover, heating becomes more uniform if the autoclave is rotated in the microvawe owen. Thus, stationary processes are completely eliminated due to fast heating and working temperature can be achieved in minutes and maintained constant by controlling the magnetron emision power. Thermal agitation and chemical activation induced by electromagnetic radiation increases the reaction speed, nucleation centers numbers are higher and convection currents efficiently replenishe nuclei with fresh nutrient. In this way, nanoparticles will be produced having low dimensional dispersion due to the high speed of recrystallyzation, a large number of nanoparticles growing simultaneously and very fast.

METHOD OF OBTAINING AG-DOPED TIO_2 NANOPARTICLESSYNTHESIZED THROUGH M-H

Into a Berzelius glass 40 ml of ethyl alcohol were added, on top of which 10 ml of titanium

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isopropoxide under continuous stirring were droped. After a few minutes of continuous stirring, 45 ml of double distilled water were added.

The initial pH of the solution was 5.5 and the adjustment to the final pH (according to the experimental design) was obtained with nitric acid. Then a nutrient, silver nitrate, was added. When titanium isopropoxide is added on ethyl acid, a solid white precipitate is obtained. Before thermal treatment, the precipitate was washed with distilled water, filtered and dried at 600˚C for 10 hours. There were performed preliminary experiments, synthesized Ag doped TiO_2 probes and controlled factors are presented in Table 1.

Table 1. Parameters of Ag doped TiO_2 probe synthesized through M-H

Samples	Ag concentration [%]	Autoclaving duration [min]	Autoclaving temperature [^{0}C]	Microwave owen power [W]
P1$_{M\text{-}H}$ (15-150-800)	2	15	150	800
P2$_{M\text{-}H}$ (30-150-800)	2	30		
P3$_{M\text{-}H}$ (15-200-1000)	2	15	200	1000
P4$_{M\text{-}H}$ (30-200-1000)	2	30		
P5$_{M\text{-}H}$ (15-150-800)	3	15	150	800
P6$_{M\text{-}H}$ (30-150-800)	3	30		
P7$_{M\text{-}H}$ (15-200-1000)	3	15	200	1000
P8$_{M\text{-}H}$ (30-200-1000)	3	30		

After autoclaving, the obtained material was filtered and washed with distilled water in order to remove secondary reaction compounds. The filtered and washed material was dried at 60˚C for 6 hours.

Verification of the presence of Ag ions in the washing solution has been done by using calcium chloride. No AgCl precipitate has been observed, thus meaning that all Ag quantity has been consumed in reaction.

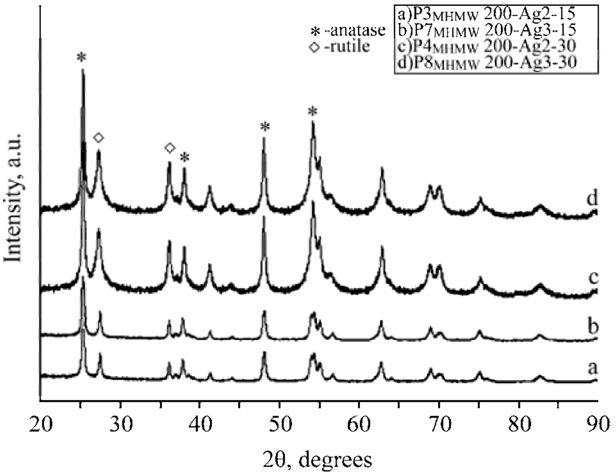


Fig. 1. XRD spectra for P3$_{M\text{-}H}$ 200-Ag2-15 (a), P7$_{M\text{-}H}$200-Ag3-15 (b), P4$_{M\text{-}H}$ 200-Ag2-30 (c) and P8$_{M\text{-}H}$200-Ag3-30 (d), synthesized through M-H.

X-ray diffraction (XRD) spectra for Ag-doped TiO_2, autoclaved at temperatures of 150˚C or 200˚C for 15 and 30 minutes, synthesized through M-H, are presented in Figs. 1 and 2. In autoclaving at 200˚C for 15 minutes, a phase transition is taking place for TiO_2 doped both with 2% Ag (Fig. 1a) and with 3% Ag (Fig. 1b), resulting in a mixture of anatase and rutile phases.

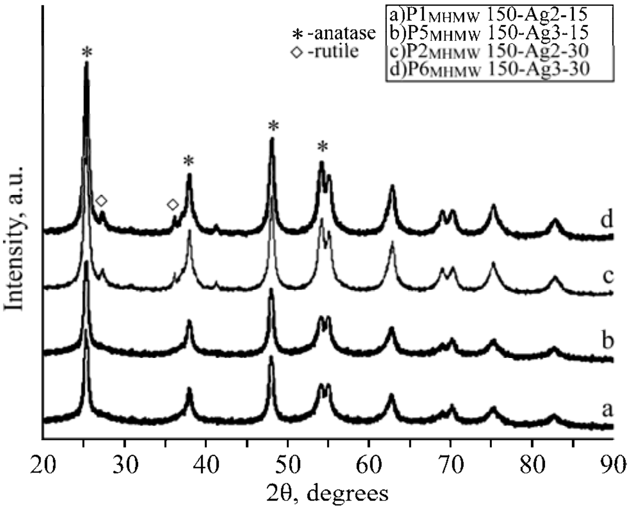


Fig. 2. XRD spectra for P1$_{M\text{-}H}$ 150-Ag2-15 (a), P5$_{M\text{-}H}$ 150-Ag3-15 (b), P2$_{M\text{-}H}$ 150-Ag2-30 (c) and P6$_{M\text{-}H}$150-Ag3-30 (d), synthesized through M-H.

When autoclaving duration increases up to 30 minutes, anatase becomes more unstable and phase transition is more pronounced (Figs 1c and 1d).

In autoclaving at 150˚C for 15 minutes, for both TiO_2 doped with 2% Ag (Fig. 2a) and with 3% Ag (Fig. 2b), a single crystalline phase is obtained, namely, anatase.

After autoclaving for 30 minutes, at the same temperature of 150˚C, anatase phase passes progressively into rutile one (Fig. 2c and 2d). With the spectral analysis, it is noted that there are no significant changes in the crystalline phases irrespective of the amount of a dopant.

Table 2. Average dimensions of Ag doped TiO_2 nanoparticles sytnhesized through M-H

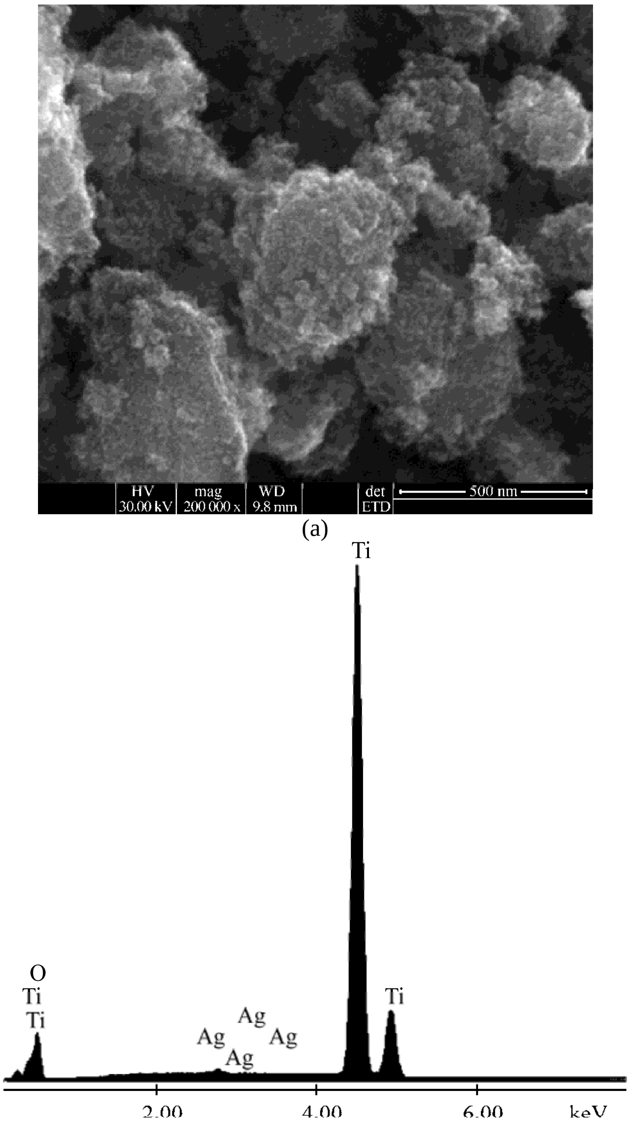
Material type	Nanoparticles dimension (nm)
P4$_{M\text{-}H}$ (30-200-1000)	10.1
P8$_{M\text{-}H}$ (30-200-1000)	9.9

The conclusion drawn from these results is that the structure and crystalline form of Ag-doped TiO_2 nanoparticles sytnhesized through M-H are, in the first case, influenced by the dopant quantity, thermal treatment and autoclaving parameters. In Table 2 the average dimensions of nanoparticles are presented, calculated with the Debye-Scherrer equation (relation 1) [2]:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \qquad (1)$$

where: λ – the wavelength of the X-ray radiation (λ = 0.15406 nm); *K* – the Scherrer constant

(K = 0.89); θ – the diffraction angle; β – the line width at half maximum height for differnt peaks from diffractogram.



(a)

(b)

Fig. 3. SEM surface morphology (a); EDAX spectrum (b) for $P4_{M-H}$ (30-200-1000).

Figure 3 presents the SEM image and EDAX spectrum for TiO_2 doped with 2% Ag synthesized through M-H.

APPLYING TAGUCHI ROBUST DESIGN FOR DIMENSIONAL STABILITY OF AG-DOPED TIO_2 NANOPARTICLES

A design of experiments usually consists in performing a fixed aprioristic number of experiments in order to determine, with minimum attempts and maximum precision, possible influences of different factors on optimization of a system performance [1].

Based on the initial results, it has been decided to use the Taguchi L_8 experimental design, consisting of an orthogonal fractional factorial design. An orthogonal fractional factorial design consists of much fewer experiments than a full factorial design but its drawback is offering a smaller amount of information.

Thus, besides the four control factors determined initially: dopant (Ag) concentration, autoclaving duration, autoclaving temperature and microwave owen power, three more factors were added: nutrient quantity, pH of the solution and autoclave filling degree.

The actual design consisted of 8 experiments on which 7 factors were studied at 2 levels, the system response (to be improved) considering nanoparticles dimensions, as shown in Table 3[4].

Table 3. Control factors and levels

No.	Description of factor	Level 1	Level 2
1	Dopant (Ag) concentration	2%	3%
2	Autoclaving duration	15 min	30 min
3	Autoclaving temperature	150°C	200°C
4	Microwave owen power	800 W	1000 W
5	Nutrient quantity	10 g	20 g
6	Solution pH	2.5	2.8
7	Autoclave filling degree	50%	60%

The objective of these 8 experiments was to determine the best combination of factors in order to achieve dimensional stability of Ag-doped TiO_2 nanonanoparticles, according to the target value of 10 ± 0.2 nm.

Using Qualitek-4 statistical package experimental conditions were randomly established. The experiments were performed, results (nanoparticles dimension) obtained in 8 experiments. The corresponding S/N (Signal/Noise) ratios are presented in Fig. 4. Actual values were: General mean = 9.987 nm, Standard deviation = 0.132, Average S/N ratio 17.806 dB.

By analyzing average effects of the factors on the S/N ratio and their interactions, the optimal condition was determined, as shown in Table 4.

In order to determine the influences of significant factors, a variance analysis was performed, namely ANOVA. Under analysis were optimal and performance conditions, with the due account of the comparison of parameters of current and improved conditions. It was also established that the factor "Solution pH" is not statistically significant and therefore can be eliminated from the model (actually it can have any of the two levels). The order of factors importance and corresponding percentage are presented in Table 5.

In addition, two confirmation experiments (with factor's levels as previously determined) were also performed, thus presenting the statistical parameters of experiments and their capability indices.

The calculated values presented in Table 6 are those for optimum condition, which are consistent with those calculated in average effects and interactions of factors [3].

Conditions	Sample # 1	Sample # 2	Sample # 3	Sample # 4	Sample # 5	Sample # 6	S/N Ratio
Trial # 1	9.85	9.79	9.88	9.94	9.85		16.691
Trial # 2	10.11	10.18	9.98	9.96	9.92		19.755
Trial # 3	9.81	9.83	9.82	9.9	9.87		16.044
Trial # 4	10.12	10.18	10.17	10.17	10.11		16.318
Trial # 5	9.94	10.14	10.12	10.19	9.98		18.291
Trial # 6	9.8	9.89	9.87	9.91	9.92		17.772
Trial # 7	10.18	10.12	9.93	9.89	9.86		17.778
Trial # 8	10.12	9.98	10.14	10.12	9.94		19.796

Fig. 4. Experimental results and S/N ratios.

Table 4. Optimal condition based on average effects of factors

Factors	Level
Dopant (Ag) concentration	2
Autoclaving duration	2
Autoclaving temperature	1
Microwave owen power	2
Nutrient quantity	2
Solution PH	2
Autoclave filling degree	2

Table 5. Order of factors importance

Order of importance	Factors	Percentage [%]
1	Autoclave temperature	26.869
2	Autoclave filling degree	24.368
3	Microwave owen power	20.096
4	Dopant (Ag) concentration	20.020
5	Autoclaving duration	5.687
6	Nutrient quantity	2.901
7	Error/other	0.391
		TOTAL = 100%

Factors total contribution is 3.12; performance current general average for S/N ratio = 17.806 dB; an expected result at optimum conditions for S/N ratio = 20.927 dB. For a confidence degree of $P = 95\%$ (significance level $\alpha = 1-P = 5\%$), confidence interval Δ is calculated according to relation (2):

$$\Delta = \pm\sqrt{\frac{F\left(n_1, n_2\right)\cdot V_e}{N_e}} \qquad (2)$$

where: $F(n_1, n_2) = 1.6$ (calculated value), $n_1 = 1$ (error degree of freedom), $n_2 = 1$, $V_e = 0.00816$ (error variance), $N_e = 1.14$ (replications number), factors degree of freedom (dgf = 6) as included in estimation.

The value of $\Delta = \pm\ 0.107$ resulted for a confidence interval and therefore an expected value for S/N ratio at optimum of 20.927 ± 0.107, meaning a confidence interval of [20.820; 21.034]. Thus, the expected value expressed in quality characteristics (nanoparticles dimension) units, based on S/N ratio of 21.034 (optimum value), is $Y_{\text{expected}} =$ $= 10 \pm 0.089$ nm, meaning a confidence interval of [9.911; 10.089] nm.

Another way of showing performance improvement is to present modifications which occur in normal distribution. Thus, an improved S/N ratio at the optimum condition corresponds to a reduction in the standard deviation.

Figure 5 presents the normal distribution for current and improved conditions assuming that the optimum performance is a target; control limits are at ± 3σ at improved condition, standard deviation is directly proportional to the S/N ratio modification.

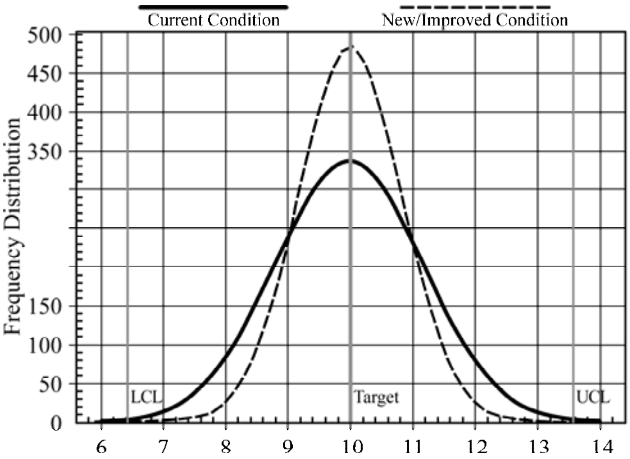


Fig. 5. Variation reduction plot for improved conditions based on normal distribution.

Table 7 presents, by comparison, the parameters situation at current and improved conditions.

Table 7. Parameters values at improved versus current conditions

Initial experiment	Current conditions	Predicted conditions
S/N ratio	17.806	20.927
Mean	9.987	10
Standard deviation	1.19	0.83
Cp	1	1.432
Cpk	0.996	1.432
Savings	–	51.2 cents/1$ loss

In order to determine whether the error made in fractioning the experimental design (8 experiments), a full factorial simulation ($2^7 = 128$ experiments) was performed. There is a possibility to work with predefined equations that can be solved in complete factorial conditions (all possibilities). The following notations were used: *Y* – Nanoparticles dimension; *A* – Dopant concentration; *B* – Autoclaving duration; *D* – Autoclaving temperature; *E* – Microwave owen power; *F* – Nutrient quantity; *G* – Solution pH; *F* – Autoclave filling degree. Assumnig that the characteristic equation represents the system behaviour, the maximum value obtained from the full factorial experiment combinations may be considered as an exact solution with which the solution obtained from L_8 experiment can be compared. Also, performance at optimum conditions can be compared with an exact solution in order to determine the L_8 experiment prediction correctness.

More than 2000 simulations were performed and the obtained linear characteristic equation is presented in relation (3) as borrowed from [7]:

$$\begin{aligned} Y &= 0.425\cdot A + 0.025\cdot B + 0.001\cdot C + 0.00225\cdot D + \\ &+ 0.045\cdot E + 0.485\cdot F + 0.04575\cdot G. \end{aligned} \tag{3}$$

Table 8 visualizes a comparison between the calculated values obtained from the full factorial experiment simulation and the values obtained from L_8 experiment. One can notice that the maximum relative error is -3.87%

Table 8. Values comparisons between full factorial experiment simulation and L_8 experiment

Full factorial simulation experiment number	L_8 experi-ment number	Calculated value (simula-tion)	Average value calculated (L_8)	Relative error [%]
1	1	9.48	9.862	- 3.87
16	2	9.98	10.030	- 0.49
52	3	9.95	9.846	1.05
61	4	10.25	10.150	0.98
86	5	10.31	10.074	2.34
91	6	10.00	9.878	1.23
103	7	9.87	9.996	-1.26
106	8	10.18	10.040	1.39

APPLYING RESPONSE SURFACE METHOD DESIGN FOR DIMENSIONAL STABILITY OF AG-DOPED TIO_2 NANOPARTICLES

The Response Surface Method (RSM) was applied by using a Draper-Lin small compositional design (40 experiments) in a single block (including two central points per block) with four degrees of freedom for error [6]. The regression equation of the first order model (relation 4) was determined, the results being estimated accordingly.

$$\begin{aligned} Y &= 0.966292 + 0.000378769\cdot A + 0.0006648469\cdot B - \\ &- 0.00108788\cdot C + 0.00020 - 0.00130976\cdot E + \\ &+ 0.0354602\cdot F + 0.0463939\cdot G. \end{aligned} \tag{4}$$

The main effects of factors were estimated as well as the standard deviation for each effect (which is measuring the sampling error). Table 9 presents, by comparison, the order of importance of factors, obtained through Taguchi (L_8) and RSM (Draper-Lin) designs [5].

One can see that the first 3 factors are considered as main factors (in that order) for both designs. Under analysis were predictions with the gradient method (steepest ascent method) and an optimized combination of factors levels for the Draper-Lin design [8].

Table 9. Order of factors importance obtained through Taguchi and RSM designs

Order of importance	Taguchi L_8	Draper-Lin
1	Autoclaving temperature	Autoclaving temperature
2	Autoclave filling degree	Autoclave filling degree
3	Microwave owen power	Microwave owen power
4	Dopant (Ag) concentration	Nutrient quantity
5	Autoclaving duration	Solution pH
6	Nutrient quantity	Autoclaving duration
7	Solution pH	Dopant (Ag) concentration

The estimated response surfaces and contours were presented (Fig. 6 showing the Estimated Response Surface for Ag-doped TiO_2 nanoparticles dimension as a function of the Autoclaving temperature and Autoclave filling degree, the rest of the factors being kept at their average value); besides a comparison between different estimation methods and calculations of Ag-doped TiO_2 nanoparticles dimensions are given.

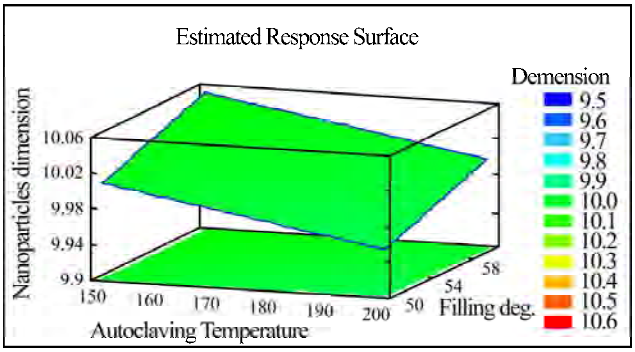


Fig. 6. Estimated Response Surface for Ag-doped TiO_2 nanoparticles dimensions – RSM (Draper-Lin) design.

CONCLUSIONS

The M-H method used to synthesize Ag-doped TiO_2 nanoparticles eliminates some of major drawbacks of other methods of synthesis. In order to achieve dimensional stability (one the most important features of Ag-doped TiO_2 nanoparticles), certain initial experiments were performed showing that there are four controllable factors that are very important. Moreover, it was established that there are three more factors with major influence on dimensional stability. In order to determine the factors order of influence upon dimensional stabiliry of Ag-doped TiO_2 nanoparticles, two different designs of experimentation were used: the Taguchi

L_8 fractional factorial design (8 experiments) and the RSM (Draper-Lin small compositional design) in 40 experiments. It has been demonstrated that the error made by using a fractional design (L_8) instead of a full factorial design (2^7 = 128 experiments) is relatively small. Moreover, the 40 experiments of Draper-Lin design demonstrated the same importance and order of factors as L_8 design.

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Реферат

Приведены результаты оптимизации параметров синтеза гидротермальным методом в СВЧ поле легированных Ag наночастиц TiO_2. Для оптимизации процесса использовались метод Тагучи (матрица L_8) (Taguchi L_8) и план второго порядка Дрейпера-Лина (Draper-Lin small composite design). Определены технологические факторы процесса синтеза, как то концентрация примеси, продолжительность и температура процесса, подводимая СВЧ мощность, состав и pH раствора, степень заполнения автоклава, влияющие на стабильность размеров легированных Ag наночастиц TiO_2. Показано, что оба использованных метода оптимизации приводит к подобным результатам.

Ключевые слова: TiO_2, Ag, легирование, оптимизация параметров синтеза, Тагучи, Дрейпера-Лина.