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EFFECT OF DIFFERENT PARAMETERS ON SONOCHEMICAL SYNTHESIZED NANOCRYSTALLINE TIO_2 PARTICLES

An ultrasonic-assisted method to directly prepare nanocrystalline TiO_2 has been used. TiO_2 was synthesized by the hydrolysis of tetraisopropyl titanate (TIPT) in the presence of de-ionized water and ethanol under high-intensity ultrasonic irradiation (24 KHz, 300 W/cm^2) at different conditions. The effect of water content, water-to-TIPT ratio, water-to-ethanol ratio and sonication time on the particle size of TiO_2 has been investigated by using design of experiment (DOE). The water content, water-to-TIPT ratio, water-to-ethanol ratio and sonication time were varied in the range 100-150 ml, 50-75% v/v, 20-30% v/v and 3-4 h, respectively. Particle size of TiO_2 was characterized using a particle size analyzer. The results of DOE show that water content has the greatest effect on the particle size of TiO_2.

Keywords: ultrasonic, parameters, nanocrystalline TiO_2, particle size, Taguchi method.

In recent years, the application of nanoparticles is getting more generalized and covering different fields including optoelectronics [1], catalysis [2], medicine [3], sensor devices [4,5], etc. Among the metal oxide nanostructures, titanium dioxide has specific chemical and physical properties that make it an attractive material for various applications such as catalysis, white pigment for paints or cosmetics, electrodes in lithium batteries [6], dye-sensitized solar cells [7], and photocatalyst [8] to deal with environmental pollution, wastewater treatment, and air purification. More recently, TiO_2 has been tested as a dielectric material for the next generation of ultrathin capacitors [9] and as a photonic crystal for photonic band-gap materials [10].

Hence, it is of great importance to improve the preparation method of nanocrystalline TiO_2. Up to now, the methods for preparing nanometer TiO_2 can be summarized as follows: sol-gel method [11], vapor decomposition of titanium alkyloxides or $TiCl_4$ in oxygen [12], hydrothermal technique [13], reversed micelle method [14], and oxidation of metallic Ti powder [15]. Sonochemistry, by which influential ultrasound is used to inspire chemical processes in liquids, is currently the focus in a wide range of chemical materials science and technology, since it causes novel chemical reactions and physical changes which do not occur unless sonically inspired. Now, nano-structured metals, alloys, oxides, carbides and sulfides, or nanometer colloids and nanostructure supported catalysts can all be prepared by using high-intensive ultrasound [16]. In this work, TiO_2 particles synthesized by hydrolysis of titanium tetraisopropyl in the presence of acoustic waves and DOE are used for investigating the effect of different parameters.

MATERIALS AND METHODS

Materials

Tetraisopropyl titanate (TIPT) with analytical purity of 99.5% (Merck), ethanol (analytical grade, Merck) and de-ionized water were used without additional purification. The molecular formula of TIPT is $Ti(OCH(CH_3)_2)_4$ and reacts with water to form TiO_2. It has a melting point and boiling point of 19 and 232 °C, respectively.

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Synthesis of TiO_2 nanoparticles

TiO_2 nanoparticles was synthesized by hydrolysis of tetraisopropyl titanate (TIPT) in the presence of de-ionized water, ethanol, and acetic acid as a dispersant under ultrasonic irradiation (24 KHz, 300 W/cm^2). In a typical synthesis, a defined volume of de-ionized water according to experimental design was mixed with acetic acid (0.15 ml) and sonicated in a sonication cell. Then, a mixture of TIPT and ethanol was injected drop-wise into the aqueous solution in 3 min. The mixture was sonicated continuously under ambient air in different times. The sonication was conducted without cooling so that the temperature was raised from 25 to about 75-78 °C at the reaction end.

Apparatus

The equipment employed in this work was a 24 kHz ultrasonic generator (UP400S), with a standard titanium horn and a 7 mm diameter replaceable flat titanium probe. The oscillator power was set at various points in a range from 40 to 80 (on a scale of 100). The acoustic power was 300 W/cm^2. For analyzing the particle size of TiO_2, particle size analyzer (SALD-2101) was used.

Experimental design

The Taguchi experimental design method is used in this study. This method reduces cost, improves quality, and provides robust design solutions [17,18].

The Taguchi method utilizes orthogonal arrays (OAs) from experimental design theory to study a large number of variables with a small number of experiments. OAs are subsets of the full factorial experiment which is balanced, *i.e.*, each variable setting occurs the same number of times and none of two experiments are the same (or even mirror images). Using OAs significantly reduces the number of experimental configurations to be studied. However, Taguchi simplified their use by providing tabulated sets of standard OAs and corresponding linear graphs to fit specific projects [19,20].

The Taguchi method has developed into an established approach for analyzing interaction effects when ranking and screening various controllable factors. Moreover, this method is applicable to solving a variety of problems involving continuous, discrete and qualitative design variables [21]. Therefore, the present study adopts the Taguchi method to investigate the main effects on ultrasonic-assisted synthesis of TiO_2 nanoparticles.

Three stages of Taguchi approach to design the experiment are as follows:

1. planning a matrix experiment (OA) based on the number control factors (preparation variables) and their alternative levels;
2. conducting the matrix experiment;
3. analyzing and verifying the results [20].

An advantage of the Taguchi method is that it emphasizes a mean performance characteristic value close to the target value rather than a value within certain specification limits, thus improving the product quality. Additionally, Taguchi's method for experimental design is straightforward and easy to apply to many engineering situations, making it a powerful yet simple tool [21]. It can be used to quickly narrow down the scope of a research project or to identify problems in a manufacturing process from data already in existence. Also, the Taguchi method allows for the analysis of many different parameters without a prohibitively high amount of experimentation [22].

Four factors, each with three levels (low, medium and high), were chosen based on the literature and qualitative experiments [22-27]. Three levels were defined for each of the factors as summarized in Table 1. An L_9 orthogonal array scheme was adapted, which needs 9 experiments to complete the optimization process [28,29].

Table 1. The results of orthogonal test L_9 (3^4)

Std.	Run	Factor 1 A: [H_2O] / ml	Factor 2 B: [H_2O/TIPT] (v/v)	Fatctor 3 C: [H_2O/Ethanol](v/v)	Factor 4 D: Sonication time, hr	Response R: Size of TiO_2, nm
1	6	100	50	20	3	295
2	1	100	62.5	25	3.5	191
3	3	100	75	30	4	174
4	5	125	50	25	4	134
5	9	125	62.5	30	3	129
6	8	125	75	20	3.5	124
7	7	150	50	30	3.5	74
8	2	150	62.5	20	4	67
9	4	150	75	25	3	62

RESULTS AND DISCUSSION

DOE Results

The experimental plan and extraction results generated using Design Expert 8, version 8.0.2.0, software is shown in Table 1. The design involves 9 runs and the response variable measured was the TiO_2 nanoparticle size.

Particle size analysis

The results of the particle size analyzer (SALD--2101) evaluation of the TiO_2 particles produced with respect to the experimental plan are shown in Table 1. Table 1 shows the average particle size of synthesized TiO_2 nanoparticles according to the orthogonal design of the Taguchi method. It is obvious that the average size of the smallest synthesized particle is equal to 62 nm.

ANOVA Analysis

The particle size of TiO_2 nanoparticles was considered as input into the Design Expert software for further analysis. In order to ensure a good model, test for significance of the regression model, test for significance on individual model coefficients and test for lack-of-fit need to be performed. An ANOVA table is commonly used to summarize the tests performed. Table 2 shows the ANOVA table for the Taguchi method. The value of "Prob > F" in Table 2 for the model is less than 0.05, which indicates that the model is significant. In this case, parameter A is significant model term. Other model parameters, *i.e.*, water to TIPT ratio (B), water to ethanol ratio (C) and sonication time (D) can be said to be insignificant. These insignificant parameters can be removed and may result in an improved model. The R^2-value calculated is 0.80, reasonably close to 1, which is acceptable. It implies that about 80% of the variability in the data is explained by the model. The predicted R^2-value is almost in reasonable agreement with the adjusted R^2. The adjusted R^2-value is particularly useful for comparing models with different number of terms. "adeq. precision" measures the signal to noise ratio. A ratio greater than 4 is desirable and indicates an adequate signal.

Although the parameter B has P-value greater than 0.05, if this parameter is entered into the model, the adj. R^2-value is higher than when only parameter A is present in the model. Therefore, both parameters A and B are entered in the model. Table 3 shows the ANOVA table according to this state.

Quantitatively, the estimated effects of a given main effect or interaction and its rank relative to other main effects and interactions is given via least squares estimation (that is, forming effect estimates that minimize the sum of the squared differences between raw data and the fitted values from such estimates). Having such estimates in hand, one could then construct a list of the main effects ordered by the effect magnitude. The half-normal probability plot is a graphical tool that uses these ordered estimated effects to help assess which factors are important and which are unimportant [29,30].

Figure 1 is a normal probability plot of the effects. All the effects that lie along the line were negligible, whereas larger ones are far from the line. Hence, the main effects including the water content (A), and water to TIPT ratio (B), have the highest effect on the size of synthesized TiO_2.

The normality of the data can be checked by plotting a normal probability plot of the residuals. If the data points on the plot fall fairly close to the straight line, then the data are normally distributed

Table 2. ANOVA Table for parameter A as a selected factor (R-squared = 0.80; adj. R-squared = 0.736; adeq precision = 6.927 (> 4))

Source	Sum of squares	dF	Mean square	F-value	P-value (Prob>F)
Model	35248.22	4	17624.11	12.15	0.0078, significant
A-A [H_2O]	35248.22	2	17624.11	12.15	0.0078
Residual	8704.67	4	1450.78	-	-
Cor total	43952.89	8	-	-	-

Table 3. ANOVA Table for parameters A and B as selected factors (R-squared = 0.89; adj. R-squared = 0.779; adeq. precision = 7.701 (> 4))

Source	Sum of squares	dF	Mean square	F-value	P-value (Prob>F)
Model	39096.44	4	9774.11	8.05	0.0399, significant
A-A [H_2O]	35248.22	2	17624.11	14.52	0.0147
B-B [H_2O/TIPT]	3848.22	2	1924.11	1.58	0.3113
Residual	4856.44	4	1214.11	-	-
Cor total	43952.89	8	-	-	-

[14]. The normal probability plot of the synthesized TiO2 nanoparticles iss shown in Figure 2. It can be seen that the data points were fairly close to the straight line and it indicates that the experiments come from a normally distributed population. Also plots of the residuals in Figure 3 revealed that they have no obvious pattern and unusual structure. They also show equal scatter above and below the *x*-axis. This implies that the model proposed is adequate and there is no reason to suspect any violation [31]. Influence of each parameter on the size of the nanoparticles is shown in Figure 4. Parameter A has the greatest effect on the nanoparticle size. By increasing the water content, the nanoparticle size is decreased. The second factor affecting the nanoparticle size is water to TIPT ratio. As this figure shows the effect of the other parameters is much less.

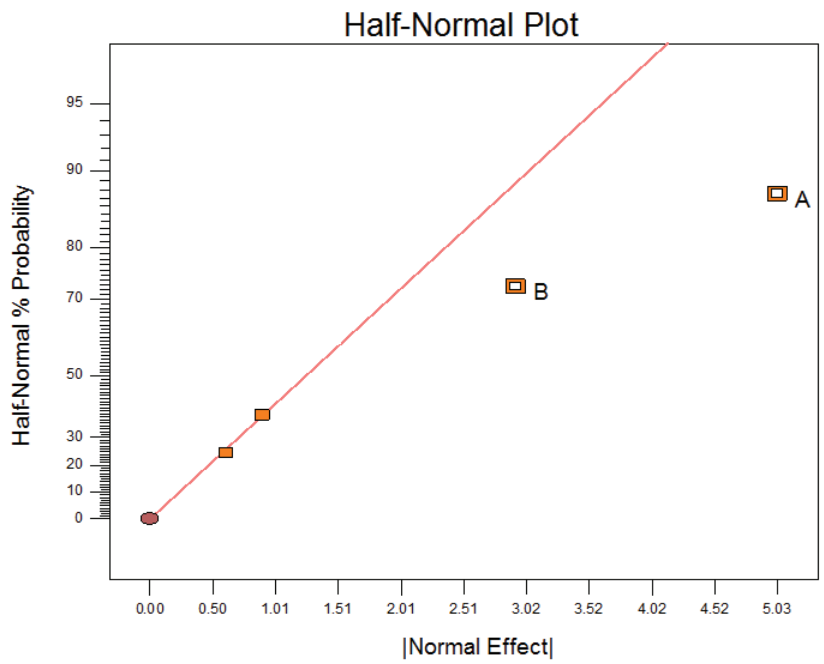

Figure 1. Half-Normal % probability vs. normal effect for each factor (A and B are the term of significant model).

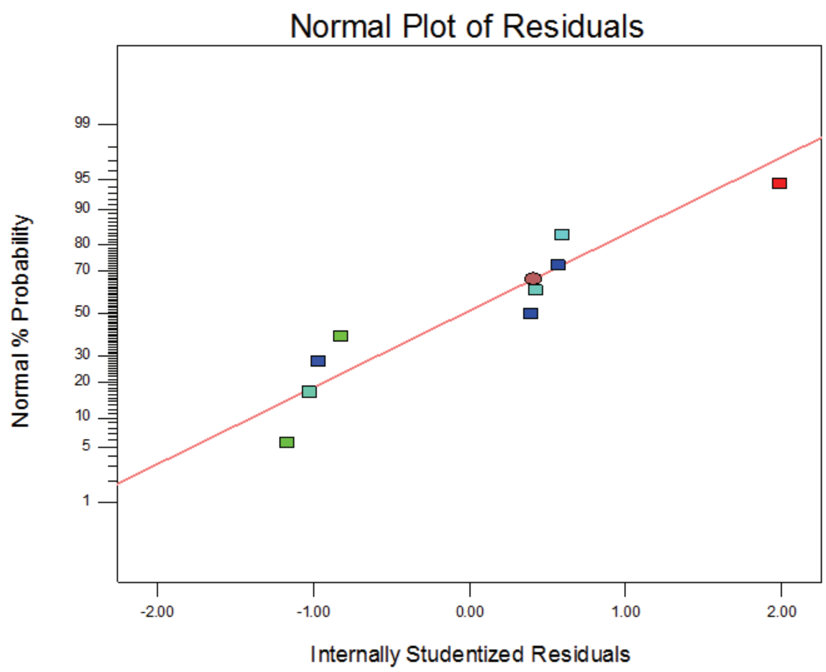

Figure 2. Normal probability plot of residual for TiO_2 particle size.

Interaction between factors

To find the interaction between the parameters, the response of each parameter against the others must be constructed. The results are shown in Figure 5. It shows the regions in which there are interactions. In each region in which the lines cross each other there is interaction. As shown in Figure 5, the collision of lines in this figure is less than it is in the other figures. This shows that parameters A and B have more effect as independent factors, while the other factors have more positive and negative interactions, which leads to less independent effect on the nanoparticle size of TiO_2.

Effect of H_2O and H_2O/TIPT

It is obvious that water plays an important role in the nucleus formation and the crystals growth. The

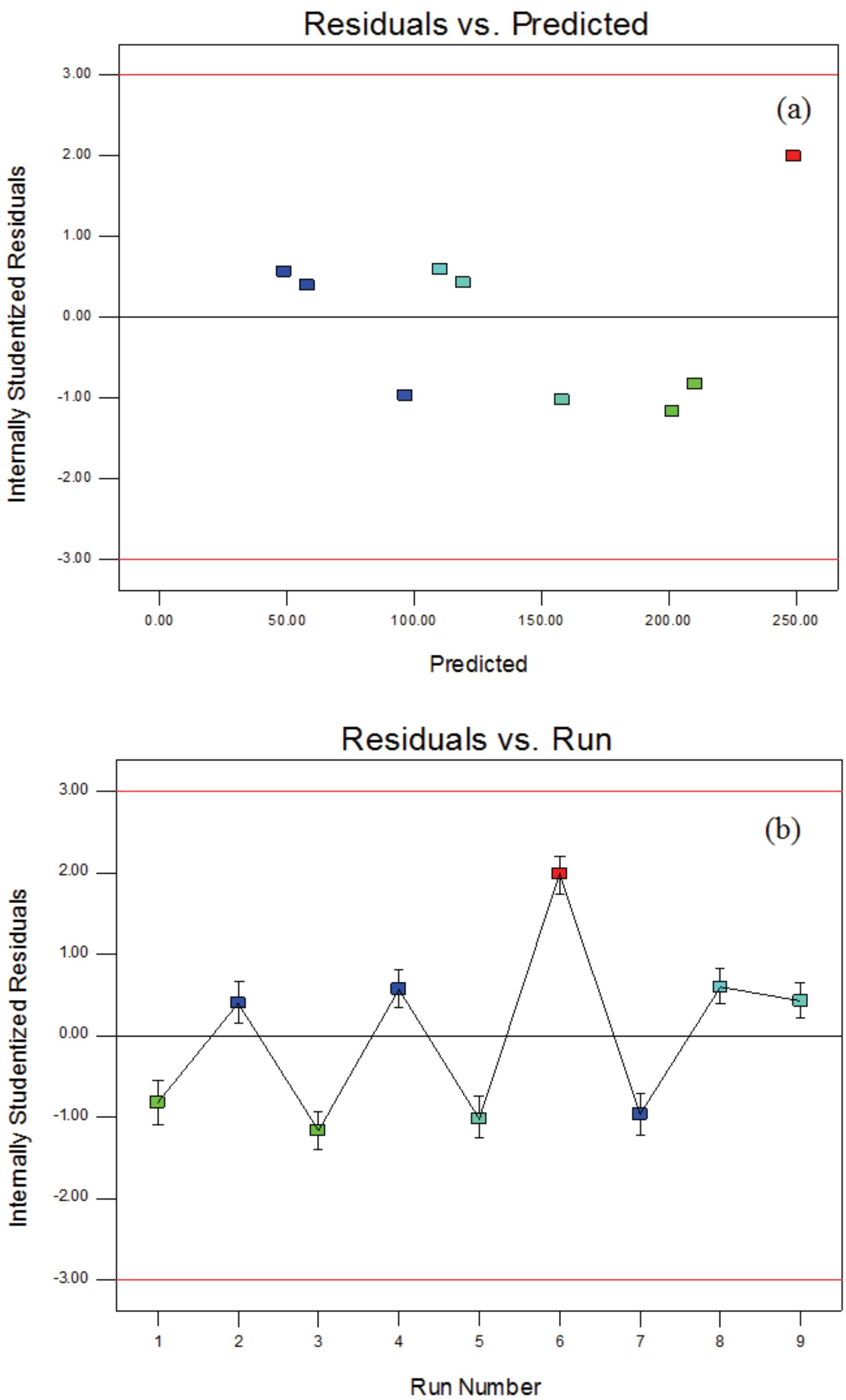

Figure 3. a) Plot of residual vs. predicted response for TiO_2 particle size; b) plot of residual vs. each run for TiO_2 particle size.

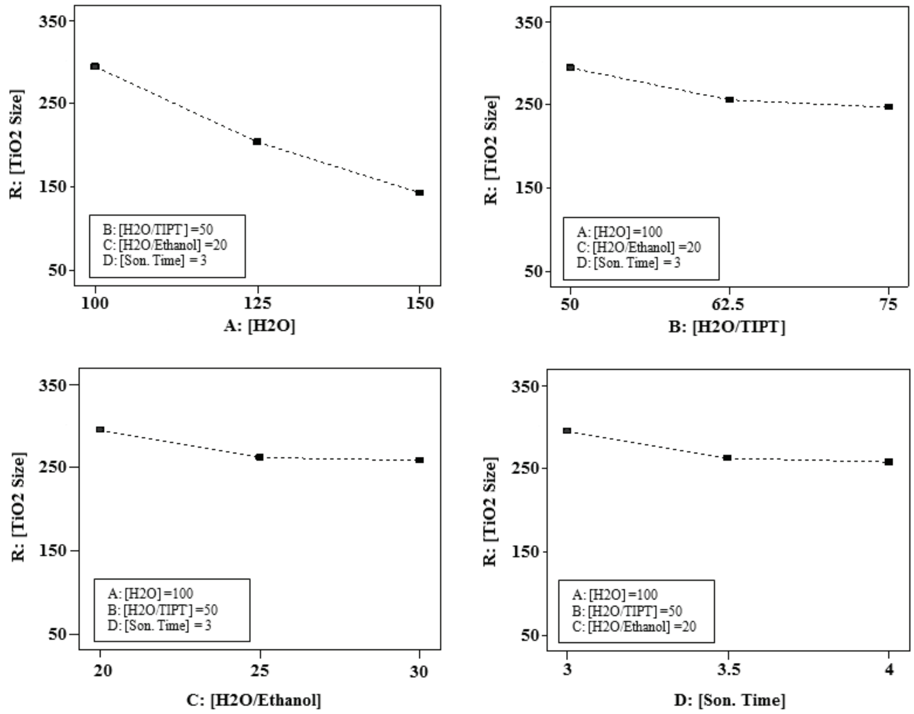

Figure 4. Effect of each main parameter on nanoparticle size of TiO_2.

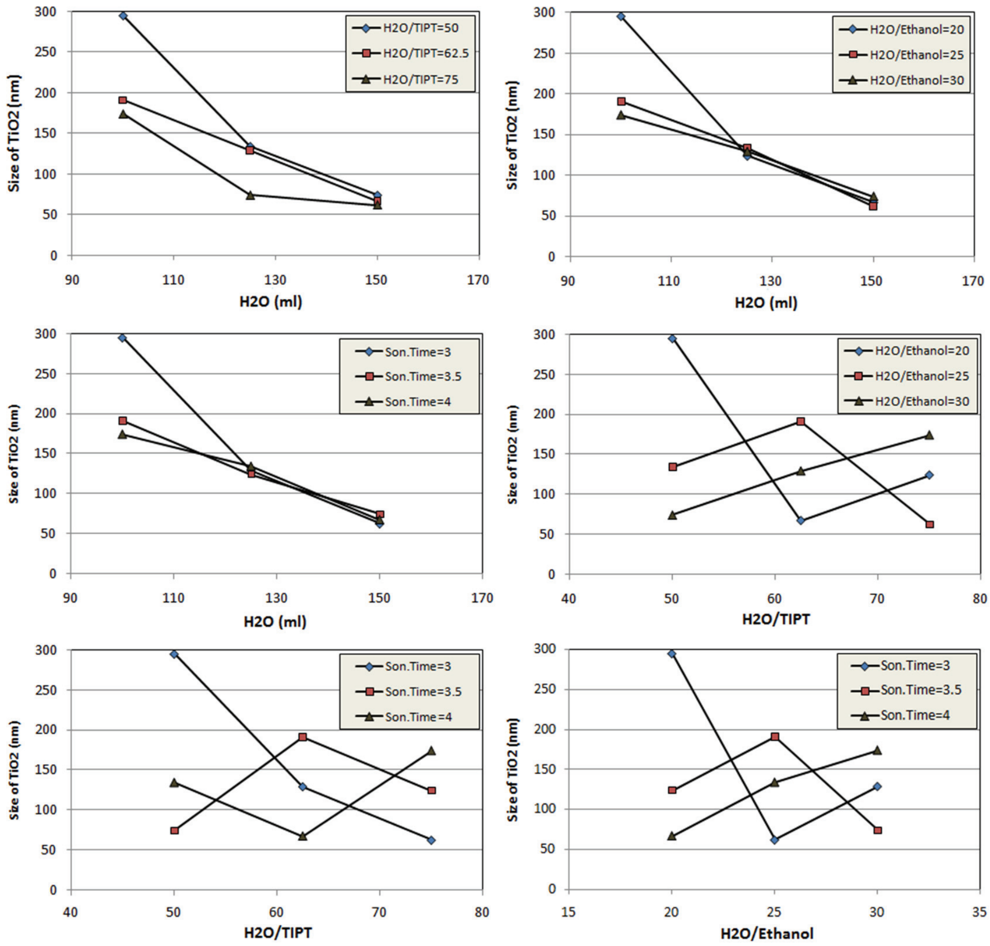

Figure 5. Binary interactions between all parameters.

nucleus can be equivalently formed in the H_2O/TIPT ratio >10 [32]. It should be mentioned that each mole of metal alkoxide needs 2 moles of water in the preparation of TiO_2 according to the following reaction:

$$Ti(OCH(CH_3)_2)_4 + 2H_2O \rightarrow TiO_2 + 4(CH_3)_2CHOH \quad (1)$$

The nucleus formation can occur readily rather than the crystals growth as the H_2O/TIPT ratio increases and this leads to the small size of the particles [32]. The DOE confirms this reality excessively. Figure 6 depicts the effect of H_2O/TIPT on the particle size of TiO_2. Also in the ANOVA table, the factor A is a significant term. This illustrates the validity of the results.

Figure 7 depicts the effect of both [H_2O] and [H_2O/TIPT] as significant factors on the particle size of TiO_2 nanoparticles as a response of DOE. It is obvious that when [H_2O] = 150 and [H_2O/TIPT] = 75, the particle size of TiO_2 becomes the smallest.

CONCLUSION

A rapid ultrasonic-assisted method has been used for the synthesis of TiO_2 nanoparticles at low temperature and high intensity. The L_9 OA of Taguchi experimental design was applied to conduct a minimum number of experiments and investigate the effect of different factors, i.e. the water content, water to TIPT ratio, water to ethanol ratio and sonication time on the particle size of TiO_2. The ANOVA revealed that the water content is significant factor that influenced the particle size of TiO_2. The model which had the higher adj. R^2-value was selected as the desirable model. Increasing the water content and water to TIPT ratio leads to smaller particle size of nanocrystalline TiO_2. Also *ANOVA* shows that parameter A has the greatest effect on the particle size of nanocrystalline TiO_2.

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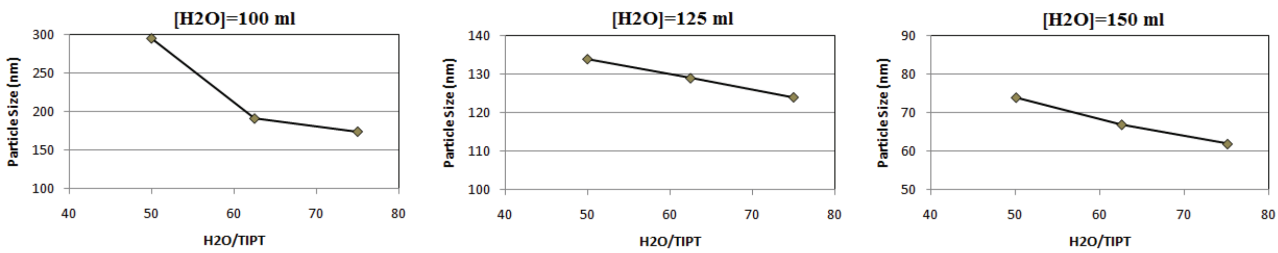

Figure 6. Effect of H_2O/TIPT on particle size of TiO_2 for different water contents.

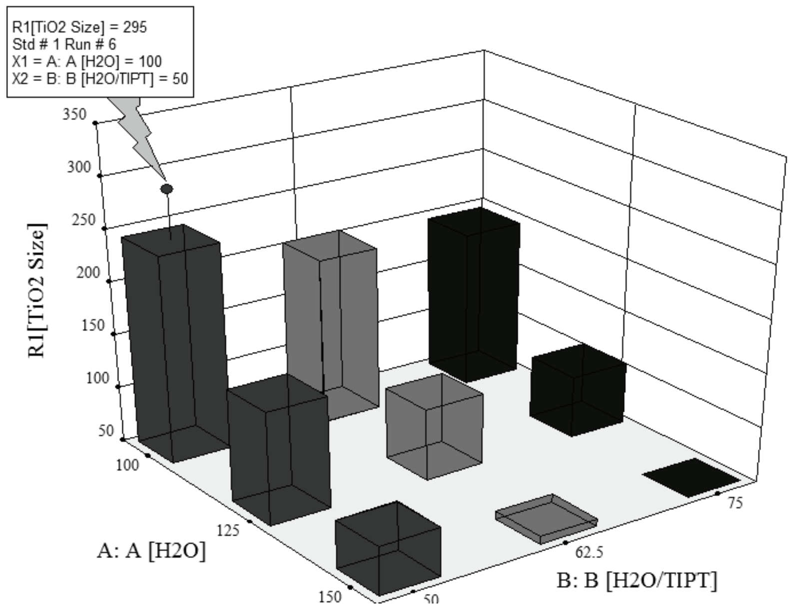

Figure 7. 3D-Plot of response R vs. factors A and B.

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NAUČNI RAD

UTICAJ RAZLIČITIH PARAMETARA NA SONOHEMIJSKU SINTEZU NANOKRISTALNIH ČESTICA TIO_2

Nanokristalni TiO_2 je pripreman ultrazvučnom metodom. TiO_2 je dobijen hidrolizom tetraizopropil-titanata (TIPT) u dejonizujućoj vodi i etanolu pod uticajem ultrazvučnog zračenja (24 KHz, 300 W/cm^2) u različitim uslovima. Korišćenjem dizajn eksperimenta (DOE) ispitan je uticaj sadržaja vode, odnosa voda-TIPT, voda-etanol i vremena sonikacije na veličinu čestice TiO_2. Sadržaj vode, odnos voda-TIPT, voda-etanol i vreme sonikacije su varirani u rasponu od 100-150 ml, 50-75% v/v, 20-30% v/v i 3-4 h, respektivno. Veličina čestica TiO_2 je analizirana pomoću odgovarajućeg analizatora. Rezultati DOE pokazuju da sadržaj vode ima najveći uticaj na veličinu čestica TiO_2.

Ključne reči: ultrazvuk, parametri, nanokristalni TiO_2, veličina čestice, Taguchi metoda.