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Synthesis and statistical analysis of changing size of nano-structured PbO_2 during mechanical milling using Taguchi methodology

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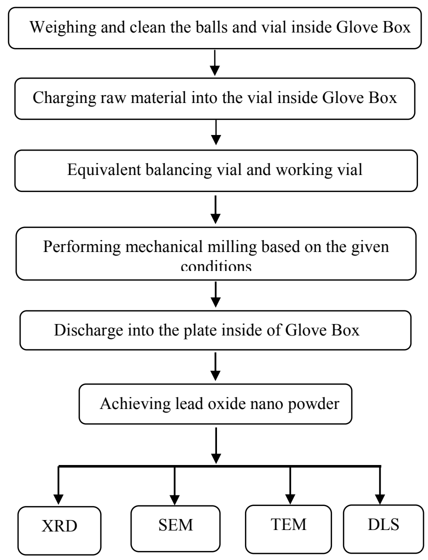
HIGHLIGHTS

- PbO_2 nano-structure was synthesized by ball milling method.
- Particle size for the nano-structured PbO_2 was about 50 nm.
- BPR parameter had the greatest impact on the size of particles.
- Minitab software revealed that the synthesis process be done in two hours.

GRAPHICAL ABSTRACT



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ABSTRACT

The research investigates synthesized nano-structured PbO_2 using ball milling. The structure and morphology of the samples were determined in the process of milling by means of XRD and SEM. The size of particles was estimated through DLS analysis. The TEM image of the synthesized powder verifies the achievement of nano dimensions. Design and analyses of the results using Taguchi methodology reveal that the size of synthesized nano-structured PbO_2 decreases as ball to powder ratio (BPR) increases while the average size of the particles increases as mechanical milling speed increases from 200 to 250 rpm. Considering the results of TEM, the particle size of the synthesized nano-structured PbO_2 by means of mechanical milling was estimated to be 50 nanometers. In addition, the even distribution and spherical morphology of the synthesized powder by this method is crystal clear in SEM images. Additionally, the result of the statistical analysis of particle size based on the effective parameters by means of Minitab software showed that BPR parameter had the greatest impact on the size of particles; BPR increase improved the objective parameter as compared with other parameters under study. According to the results obtained by Minitab software and considering the little influence of time on particle size decrease and in order to minimize the costs of synthesis, it is suggested the synthesis process be done in two hours and the BPR parameters be increased so as to decrease the size of particles.

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1. Introduction

Mechanical milling is an easy and inexpensive method to synthesize non-crystalline metals and other non-equilibrium metals [1]. The major mechanism of mechanical milling is the recurrence of cold fusion and particle breakage which result in the production of nano-structure in the course of time [2]. Mechanical milling method makes the occurrence of chemical reactions and morphological changes in normal temperatures possible by means of synthetic acceleration [3]. As a result, many materials and structures can be produced in solid state [7-3]. Simplicity of equipment, needlessness of high temperatures and the implementation of production in just one step are the properties of mechanical milling which can economize the production of many materials and alloys [8].

Since the provision of optimal nano-synthesized materials is costly and time-consuming, the use of modern designing and lab-optimizing methods can reduce costs [9]. Accordingly, many methods have been devised which can be prioritized based upon process, cost and precision [10]. One of such methods commonly used in industrial scale is the Taguchi method which is generally applied as a practical one by various industries to improve the quantity and quality of products [11].

The purpose of this study is to synthesize the nano-structured PbO_2 by means of mechanical milling and to investigate the impacts of milling time, ball to powder ratio and the speed of milling process via Taguchi method. To investigate the micro-structure, particle distribution and surface morphology of this nano-structure, XRD, DLS and SEM were used. Also, to ascertain the achievement of nano-structure, TEM was applied. Eventually, the impact of effective parameters on the size of particles during the process of mechanical milling was administered via DLS analysis.

2. Experimental activities

2.1 Preparation of samples

8 samples including PbO_2 and commercial acetone purchased from Merck Company were applied. Mechanical milling was performed in a Fritsch Pulverisstte 5 planetary ball-mill. The vial and ceramic balls are made of alumina. To prevent unwanted reactions, all the steps of the experiment including the charging of raw materials to the vial, the placement of vial inside the miller and eventually the extraction of final product were administered under controlled argon atmosphere (Glove Box). In order to avoid an excessive temperature rise within the vial, 60 min ball milling was followed by a 10 min cooling interval. The design and analyses of tests was conducted by means of Taguchi method and Minitab software (version 17) considering three factors namely time, speed and BPR. The milling conditions are summarized in Table 1:

Table 1.
The conditions of the tests suggested by Taguchi method.

Sample No.	Time (h)	Speed (rpm)	BPR
1	2	200	20
2	2	200	30
3	5	250	20
4	5	250	30
5	2	250	20
6	2	250	30
7	5	200	20
8	5	200	30

The temperature of the laboratory was retained between 23 to 28°C. Raw materials were measured by means of a digital scale with a precision of 0.001 gram in a place which was absolutely hygienic. Also each experiment was repeated at least three times and the mean values were reported in the Table 2.

2.2 Micro-structure properties

The analysis of XRD was administered by means of XRD device D8 Advance model using Cu-Kα (λ=1.5418Å) latitude 2θ from 20 to 60 degrees. The width of X-Ray diffraction is affected by the size of crystallite and internal strain [12]. The analysis of particle size distribution was done prior to and following every stage by means of DLS in order to know the particle size and compare with the subsequent stage and to choose optimum and optimal synthesis conditions. In addition, the morphology of the nano-structured synthesized PbO_2 was investigated through SEM kyky EM3200 model. Also, to verify the achievement of nano-structure an image was taken of the synthesized particle by means of TEM.

3. Results and discussion

3.1 Results obtained by mechanical milling

The patterns of X-ray diffraction which belong to raw powder and milled powder in test 4 (after 5 hours of milling at 250 rpm and BRP 30) are shown in Figure 1. The obtained picks were compared with PbO_2 picks by means of X'pert HighScore. The results clearly show that by means of mechanical milling it is possible to obtain nano-structured PbO_2 from micron PbO_2 powder without a change in phase.

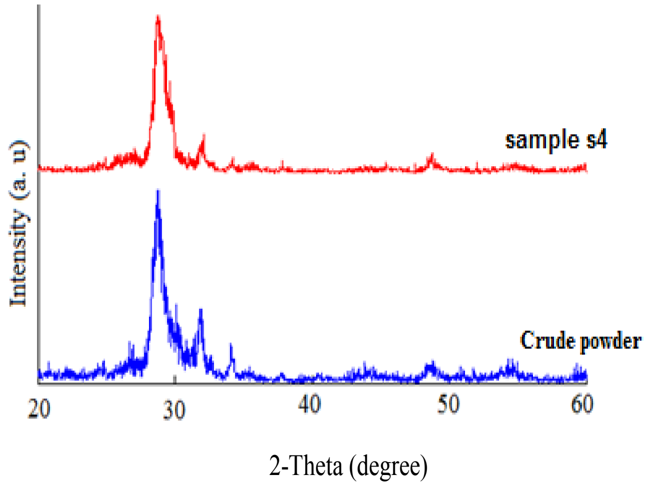

Fig. 1. The patterns of x ray diffraction in various states of mechanical milling.

Generally speaking, Figure 1 illustrates the spread, displacement and pick intensity decline as the time of mechanical milling rises. The spread of picks as milling time increases shows the decline of particle size [13]. To sum up, as time increases in mechanical milling, the picks become wider and their relative intensity declines. In order to further investigate size changes during the process of mechanical milling, DLS analysis was administered on all samples the results of which are summarized in Table 2.

By investigating Table 2, it can be concluded that the decline in particle size happened faster in the initial stages of mechanical milling, becoming slower in subsequent stages. The reason is that as the particle size declines and the borders widen, the ratio of surface to particle volumes becomes bigger and the number of atoms over the surface become larger; therefore, the number of free bonds in atoms increases and the average power which every atom receives from another declines and this causes the increase of network parameter in smaller particles. Furthermore, as BPR increases, on average, less powder mass is placed between balls in every hit, putting more strain on the powder from the balls and declining the size of particles.

Microscopic images of SEM samples prior to and following mechanical milling are shown in Figure 2. According to the images, following the milling, the size of nano-structure declines significantly with more evenness which is caused by an increase in the number of ball strikes and energy rise obtained from the balls in the process of mechanical milling. The morphology of the synthesized nano-structure is spherical and semi-spherical sized 100 nanometer on average which is one of the most ideal morphologies for applications such as battery industries due to having high surface to volume ratio in sphere shape.

Table 2.
The size of synthesized nano-structured particle by means of DLS analysis in various states of mechanical milling.

Sample No.	Time (h)	Speed (rpm)	BPR	Particle Size (nm)
0	0	0	0	1535
1	2	200	20	824.2
2	2	200	30	354.6
3	5	250	20	957.1
4	5	250	30	329.0
5	2	250	20	765.2
6	2	250	30	675.5
7	5	200	20	868.1
8	5	200	30	491.1

Figure 3 shows TEM image of PbO_2 over a course of five hours, with a BPR ratio of 30 and speed of 250 rpm. As can be seen in the picture, nano PbO_2 particles have spherical morphology. The particles are spread over an area of 20 to100 nanometer and the average nano-structure of the synthesized PbO_2 is 50 nanometer. The reason for the difference in TEM and SEM is that, during the investigation, preparation by TEM was done by means of Ultrasonic device and the particles were separated and consequently the irregular shape which is discernible through DLS is removed by Ultrasonic device and hence a better and clearer image. In addition, the reason for the difference in the size of particles by means of TEM and SEM can be attributed to the fluid ethanol film over the particles used as solvent in DLS analysis. Hence the reported amount is more accurate when done but the costly TEM analysis.

The results of test analysis by means of Taguchi method are shown in Figure 4. Based on the image, as BPR increases, the average nano-particle size declines. The reason is that the increase of BPR causes less powder mass to be placed among balls in every strike. As a result, more energy is placed upon powder on the part of balls, making the particles smaller. Also, according to this image, there is no significant change in particle size after two hours, and not only will that not decrease particle size, but the average size in all tests is very insignificant, showing the rise in milling time causes the phenomenon of cold fusion to defeat breakage.

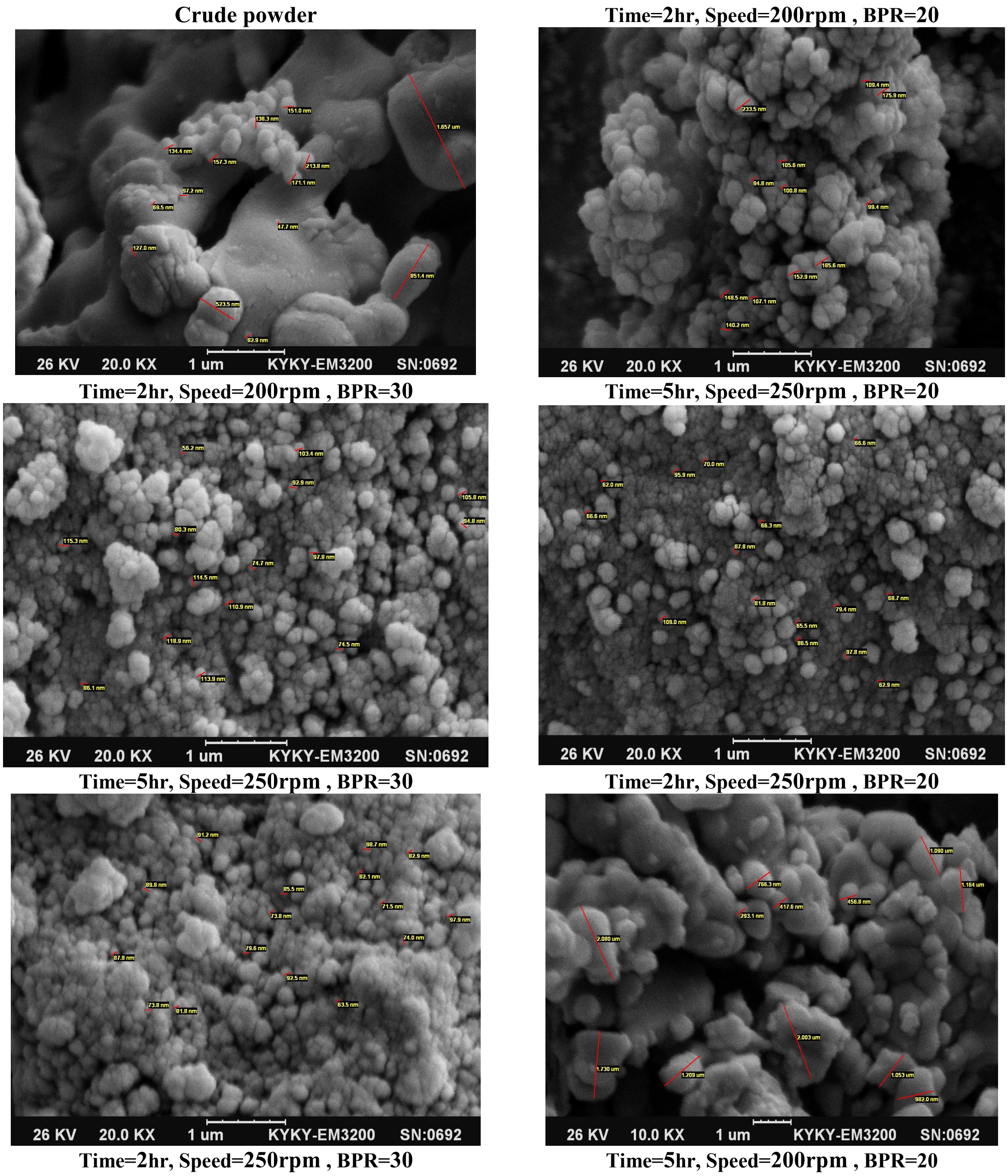

Fig. 2. SEM images of PbO_2 in various mechanical milling states.

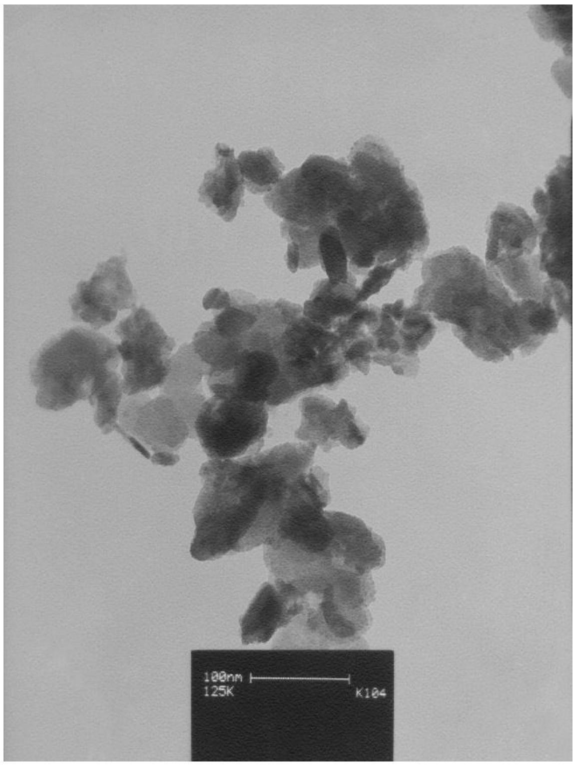

Fig. 3. TEM image of PbO_2 powder over 5 hours of mechanical milling, speed= 250 rpm and BPR=30.

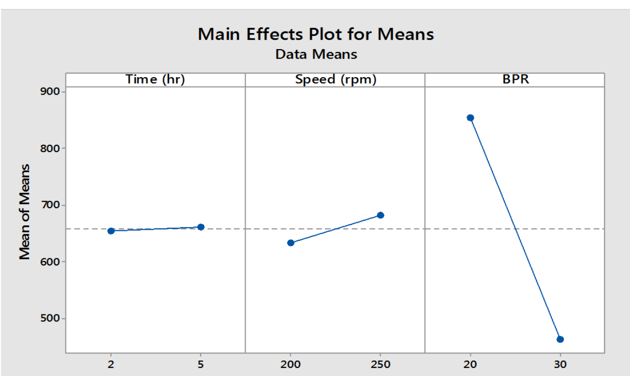

Fig. 4. The results of the average effect of the parameters under study on the average particle size.

Figure 5 illustrates the results of optimization analysis on the data in Table 2. According to this image, in which the parameters have been investigated in similar scales, the slope of every graph shows the effect of that parameter on the size of the particle. The parameter goal for the software should be defined as smaller is better. According to Figure 5, the BPR parameter has had the greatest effect in particle size change with BPR increase improving the goal parameter compared with other variables in question. The reason is that as BPR increases, on average, less powder mass is placed between balls in every strike; therefore, more energy is placed over the powder on the part of balls, making the particles smaller.

By means of a comparison between these results and raw powder analysis, it can be concluded that a decline in the size of particles occurs in the first two hours and an increase in the time of mechanical milling more than that causes the process of cold fusion to defeat breakage. According to the results in these images, it is suggested that the synthesis process be done in two hours in order to minimize synthesis costs and when needed the BPR parameter be increased to decline the size of particles.

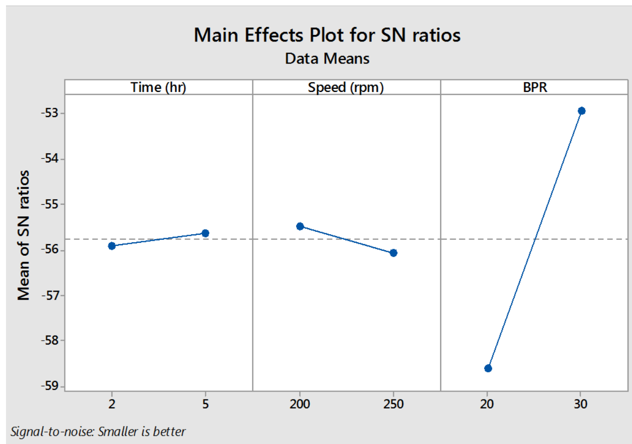

Fig. 5. The results of the average effect of the parameters under study on the average particle size.

4. Conclusions

The structure, size and distribution of particles and synthesized nano-structured morphology by means of XRD, DLS, SEM and TEM were investigated. The results of XRD clearly reveal that it is possible to obtain nano-structured PbO_2 from PbO_2 without a change in phase by means of mechanical milling. According to the results of XRD, it was revealed that when the time of mechanical milling increases, the size of particles decreases. TEM image displayed a united distribution of the synthesized particles. Based on the reported results, in this image, the particles were spread in the range of 20 to 100 nanometer and the average synthesized nano-structured PbO_2 was 50 nanometer. In addition, the results of sample analysis, obtained through Minitab software, showed that BPR parameter had the greatest impact on the size of particles with BPR increase improving the goal parameter compared withother variables in question. According to the results obtained via Minitab software, it is suggested that the synthesis be done in two hours to reduce costs given the little effect of time parameter on the size of particles and if needed the PBR parameter be increased in order to decrease the size of particles. The optimal results obtained by means of this method are related to size, morphology, phase and the structure of the synthesized materials the crystallite size of which was reported to be 50 nanometer through TEM analysis. The morphology is spherical and semispherical which due to having high surface to volume ratio is the most ideal morphologies for various applications such as using in battery plates.

The findings in this part of the study certify the economic justification of this method for production and application in industrial scale. The process of mechanical milling can be done in one stage and contrary to chemical methods there is no need for complicated chemical and thermal procedures.

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