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RESEARCH PAPER

Size Optimization of Silver Nanoparticles Synthesized by Gelcasting using the Taguchi Method

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ABSTRACT

In the present study, silver nanoparticles were synthesized by decomposition of $AgNO_3$ via gelcasting. Methacrylamide was used as a low toxic monomer for gel formation. Effect of monomer content (MAM), cross-linker to monomer ratio (MBAM/MAM), silver salt to monomer ratio ($AgNO_3$/MAM), duration of calcination, and temperature of calcination were investigated to optimize the size of nanoparticles. Taguchi method was applied to study the effect of gelcasting parameters on the size of silver nanoparticles. Mentioned parameters were surveyed at four levels and based on the Taguchi method 16 experiments were carried out. Silver nanoparticles were characterized, and average particle sizes were measured by SEM analysis. By using the signal to noise ratio (S/N) analysis of the results, it is revealed that monomer content is the most effective parameter on size of particles. Also, optimal values of monomer content, cross-linker to monomer ratio, silver salt to monomer ratio, duration of calcination and temperature of calcination for the minimum particle size were found to be 4.25 g (in 20 g water), 1:3, 1:15, 6 h and 650°C, respectively. An evaluation test was performed with the optimal value of parameters, and suitable agreement between the prediction and experimental results was observed.

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INTRODUCTION

Nano silver is one of the most favorable nano-sized metals in the field of new technologies. Distinct natural properties of silver along with size and shape of nano-sized silver make it an attractive material for the wide variety of applications. Due to its high thermal conductivity, nano silver has been used in nanofluid preparation [1]. Recently, silver nanoparticles have been used as promoters in formation of hydrates of methane and carbon dioxide [2, 3].

Silver is found to be an efficient antibacterial material and both in pure form, and in the compound is used for remedy of infections [4-6]. In this application, the purity of the silver or the silver compound is so important to prevent side effects of the impurities on health. Consequently, the methods of synthesis and purification of silver are crucial factors.

Silver compounds like silver chromate and silver dichromate are used as photocatalyst[7, 8] and silver thiocyanate is an important semiconductor[9].

Moreover, silver is known as a suitable catalyst for oxidation reaction and is commonly used as an active phase and an impregnate on a support [10, 11]. The use of an efficient sensor for detection of hydrogen peroxide in water has been reported [12].

Gelcasting is a method of forming and producing complex three-dimensional ceramic pieces [13].

In gelcasting, a premix solution containing monomer, cross-linker and metal compound

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solved in an organic solvent or water should be prepared [14]. An initiator is used for starting the polymerization reaction and gel formation, while a catalyst is used for promoting the rate of reaction. The 3D hollow spaces in the gel network are suitable for formation of particles in nano scale. The polymeric network is removed by heating at high temperatures and nanoparticles are obtained.

Researchers have worked on the gelcasting for synthesis of different nanoparticles with different applications. Synthesis of nano-sized particles and nanocomposites like Ag/CeO_2 [11] Al_2O_3/Ag [15], alumina–zirconia–yttria (AZY) [16] $LaCoO_3$ [17], α-Al_2O_3 [18] and Al_2O_3–SiC [19] have been reported. Acrylamide is used as the standard monomer for water based solution [14]. Acrylamide has neural toxicity [20], and has the highest health hazard rating (4 of 4)[14]; consequently the industry rejects this method [20]. On the other hand, using methacrylamide with a moderate health hazard rate is preferable [14].

In our previous work [21], successful synthesis of silver nanoparticles by gelcasting using methacrylamide as monomer was reported.

The silver nanoparticles are synthesized based on the decomposing reaction of silver nitrate. Decomposition starts at 240°C [22].

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$$

In this study the effects of monomer content, cross-linker to monomer ratio, silver salt to monomer ratio, duration of calcination and temperature of calcination on the size of particles of synthesized powder, were studied. The main target of this study was to optimize the effective parameters of gelcasting method for reaching the lowest average particle size.

Taguchi method was used for experimental design in order to reduce the quantity and costs of experiments and to find optimized values of the mentioned parameters for minimizing the particles size.

MATERIALS AND METHODS

All chemicals, including methacrylamide-(CH_2=C(CH_3)$CONH_2$)(MAM), N,N′-methylene bis acrylamide (($C_2H_3CONH_2$)$_2$$CH_2$)(MBAM), N,N,N′,N′-tetramethyl ethylene diamide ($C_6H_{16}N_2$) (TEMED) and ammonium persulfate ((NH_4)$_2$$S_2O_8$)(APS) were purchased from Merck and were used without any further purification. Silver nitrate ($AgNO_3$) was purchased from Simab Co. De-ionized water was used as solvent for making the premix solution.

Table 1. Investigated parameters and their levels

Parameter		Level 1	Level 2	Level 3	Level 4
MAM (g)	A	3.75	4	4.25	4.5
MBAM/MAM	B	1:10	1:7	1: 5	1:3
$AgNO_3$/MAM	C	1:25	1:20	1:15	1:10
Duration (h)	D	3	4	5	6
Temperature (°C)	E	500	550	600	650

Table 2. Experimental design using Taguchi method

	MAM (g)	MBAM/MAM	$AgNO_3$/MAM	Duration (h)	Temperature(°C)
T1	1	1	1	1	1
T2	1	2	2	2	2
T3	1	3	3	3	3
T 4	1	4	4	4	4
T5	2	1	2	3	4
T6	2	2	1	4	3
T7	2	3	4	1	2
T8	2	4	3	2	1
T9	3	1	3	4	2
T10	3	2	4	3	1
T11	3	3	1	2	4
T12	3	4	2	1	3
T13	4	1	4	2	3
T14	4	2	3	1	4
T15	4	3	2	4	1
T16	4	4	1	3	2

Table 3. Experiments and results

	MAM (g)	MBAM/ MAM	$AgNO_3$/ MAM	Duration of calcination (h)	Temperature of Calcination (□C)	Nanoparticles size (nm)	S/N ratio
T1	3.75	0.10	0.040	3	500	80	-38.06
T2	3.75	0.14	0.050	4	550	93	-39.37
T3	3.75	0.20	0.066	5	600	73	-37.27
T 4	3.75	0.33	0.100	6	650	54	-34.65
T5	4.00	0.10	0.050	5	650	59	-35.42
T6	4.00	0.14	0.040	6	600	75	-37.50
T7	4.00	0.20	0.100	3	550	81	-38.17
T8	4.00	0.33	0.066	4	500	58	-35.27
T9	4.25	0.10	0.066	6	550	44	-32.87
T10	4.25	0.14	0.100	5	500	56	-34.96
T11	4.25	0.20	0.040	4	650	68	-36.65
T12	4.25	0.33	0.050	3	600	62	-35.85
T13	4.50	0.10	0.100	4	600	71	-37.02
T14	4.50	0.14	0.066	3	650	68	-36.65
T15	4.50	0.20	0.050	6	500	60	-35.56
T16	4.50	0.33	0.040	5	550	63	-35.99

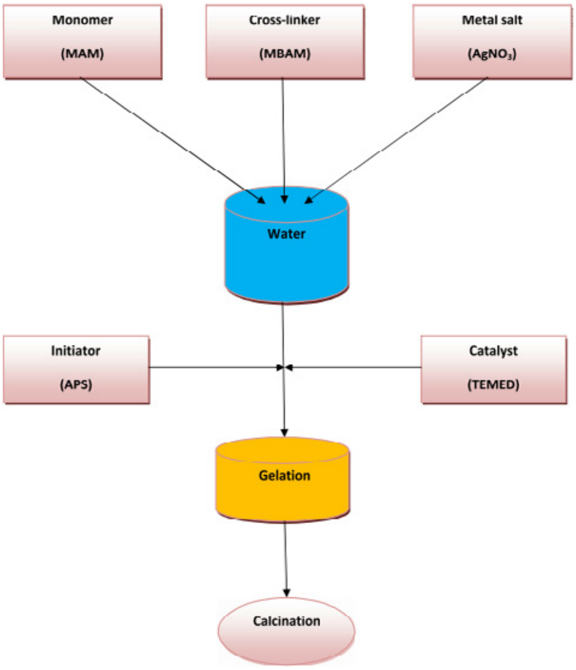

Fig. 1. Gelcasting flowchart

Experimental Design

Taguchi method was used for optimization of gelcasting parameters to synthesize the smaller particles. Five parameters were investigated to find how they affect the size of nanoparticles, and to determine which one has the main impact. Monomer content, cross-linker to monomer ratio, silver nitrate to the monomer ratio, duration and temperature of calcination were investigated as effective parameters. MAM content at four levels of 3.75, 4.00, 4.25 and 4.5 g, MBAM/MAM ratio at 1:10, 1:7, 1:5 and 1:3, $AgNO_3$/MAM ratio at 1:25, 1:20, 1:15 and 1:10, calcination duration of 3, 4, 5 and 6 h, calcination temperature of 500, 550, 600 and 650°C were investigated. Tables 1 and 2 present the parameters, their values at each level and the Taguchi proposed matrix. According to the Taguchi method, 16 experiments should be performed (Table 3). For experimental design and result analysis, Minitab software was used.

Synthesis procedures

Fig. 1 shows the procedure of gelcasting for synthesis of nanoparticles. Initially, various amounts of methacrylamide and N,N'-methylene bis acrylamide were added to 20 g of water, then silver nitrate was added to this solution. In all experiments water content was constant and the temperature was 25°C. Magnetic stirrer was used for homogenizing the solution. The solution was stirred for 30 minutes at 400 rpm. Then 8ml of APS in water solution (20 wt%) were added and immediately 1ml TEMED was introduced for accelerating the gel formation reaction. The solution was stirred at 400 rpm until the gel was formed. Then the stirring was interrupted, and the gel was left for reaction completion (Fig. 2). The obtained gel was put in the furnace at different temperatures for various durations based on the experimental design.

Fig. 2. Image of formed gel

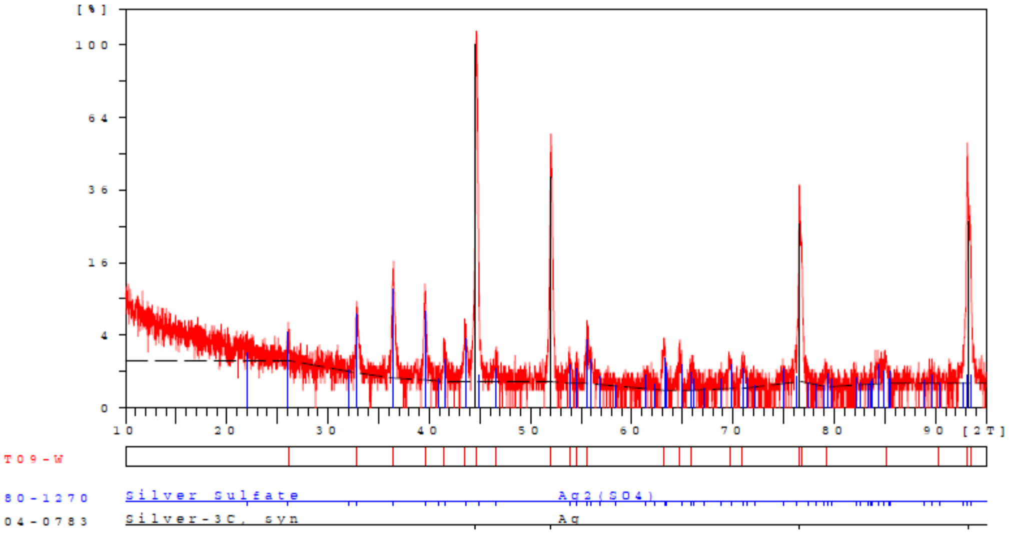

Fig. 3. XRD pattern of T9

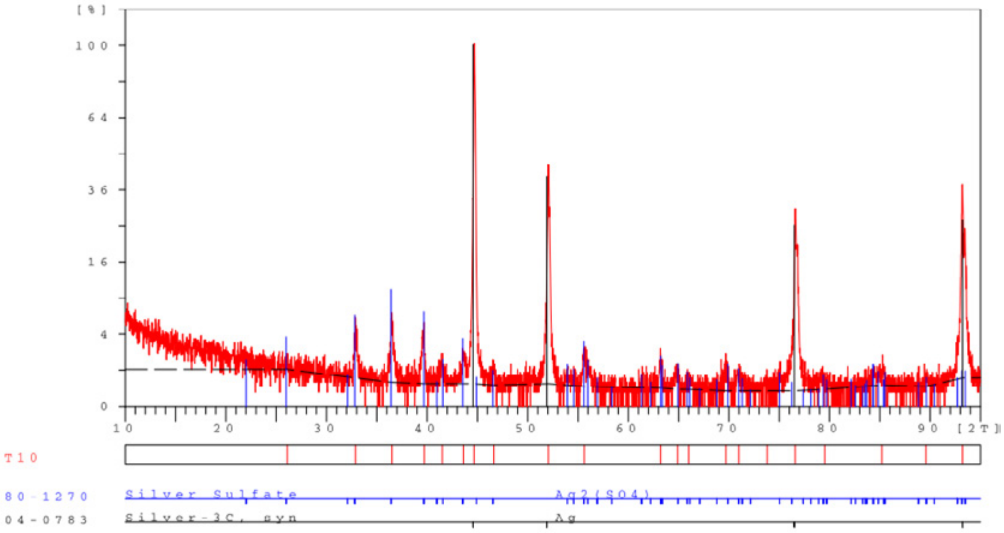

Fig. 4. XRD pattern of T10

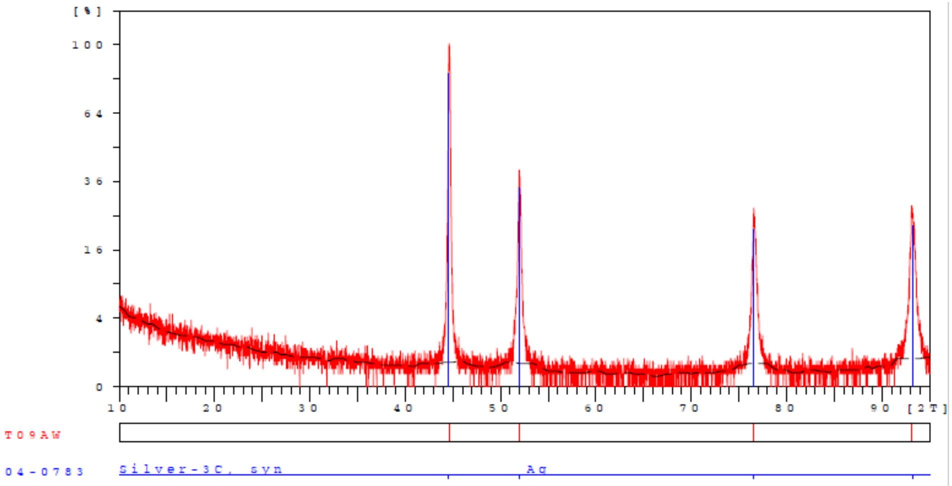

Fig. 5. XRD pattern of T9 after washing with water

RESULTS AND DISCUSSION

Sample characterization

X-ray diffraction (XRD) test for the nanoparticles was performed by a Philips set-up applying CoK_a over the 2θ range of 10–95. Figs. 3 and 4 show the XRD patterns of samples T9 and T10 after calcination. The XRD showed two phases, silver and silver sulphate. Silver sulphate might have been produced as a side product of reaction of silver and ammonium persulphate or could have been present as an impurity in the silver nitrate powder. However, silver sulphate is soluble in water and therefore, could be removed by washing with water. XRD test was done on the T9 sample after washing. Fig. 5 shows the XRD

Fig. 6. Image of a sample from T9 after washing

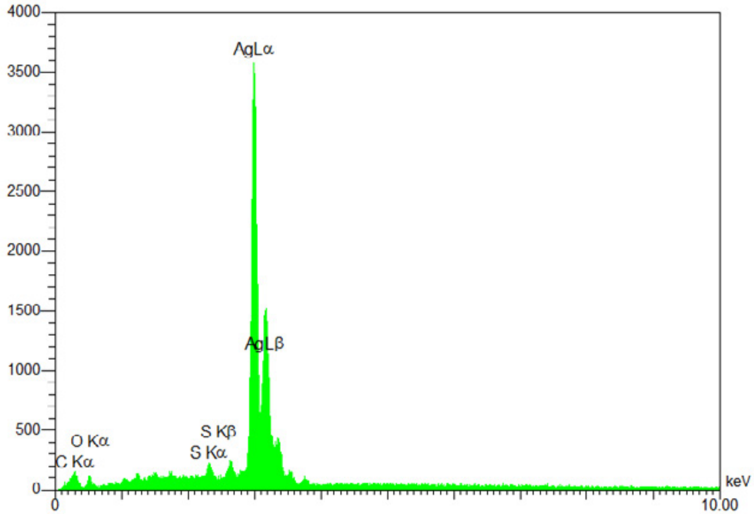

Fig. 7. EDX analysis of sample T4

pattern of sample T9 after washing. In this pattern only silver was detected, and it has shown that silver nanoparticles were synthesized without any impurity. Fig. 6 shows the silver nanoparticles after washing with water. Brilliant white metallic luster can be seen in the photo.

The elemental analysis was performed using EDX and the EDX spectrums of samples T4 and T9 are shown in Fig. 7 and 8. The EDX results revealed that the final product contained silver, carbon, sulfur and oxygen. Furthermore, EDX result of sample T4 after washing with water is shown in Fig. 9. As shown in the Fig. 9 presence of sulfur and oxygen were not detected so it could be guessed that the presence of sulfur and oxygen is related to the presence of silver sulfate in the T4 sample which removed after washing with water. The presence of carbon in the final product could be because of the remaining ash after the gel burned out.

Particles size of synthesized nanoparticles was studied by means of scanning electron microscope (SEM). Average particles size of synthesized nanoparticles were measured by using ImageJ software and reported in Table 3. Typical SEM micrographs of some of the samples (T8-T13) are illustrated in Fig. 10-15. The best result for average size of nanoparticles was 44 nm which obtained from T9. Although using other synthesis methods may result in smaller particle sizes but gelcasting is simpler and no further treatment should be used.

Transmission electron microscope (TEM) image

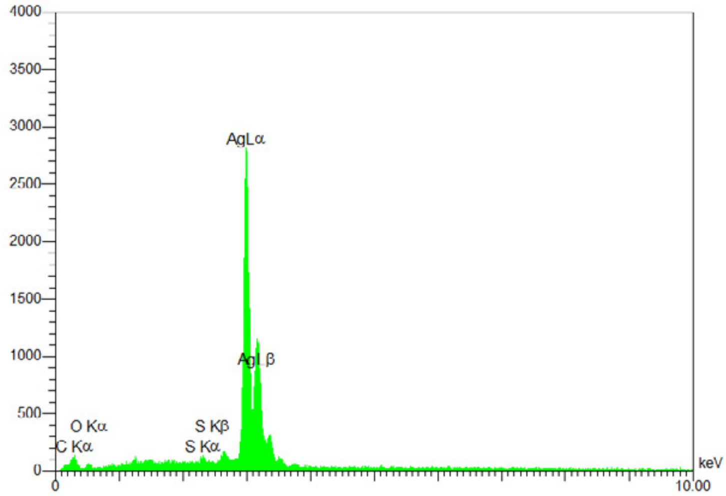

Fig. 8. EDX analysis of sampleT9

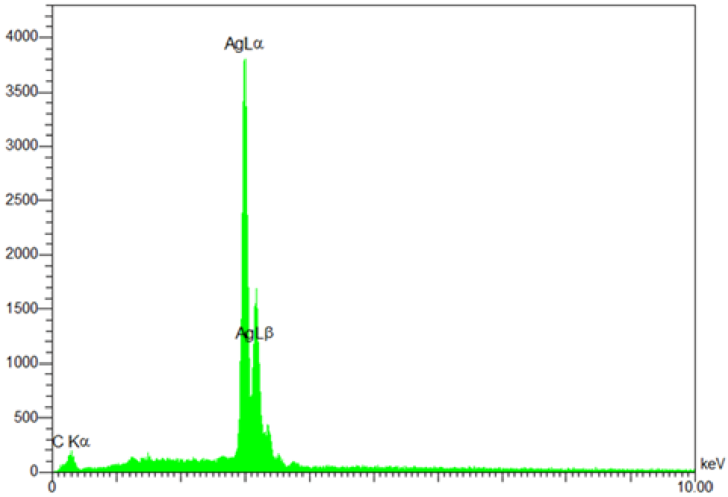

Fig. 9. EDX analysis of T4 after washing

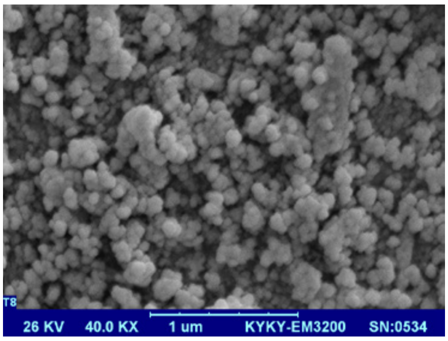

Fig. 10. SEM image of sample T8

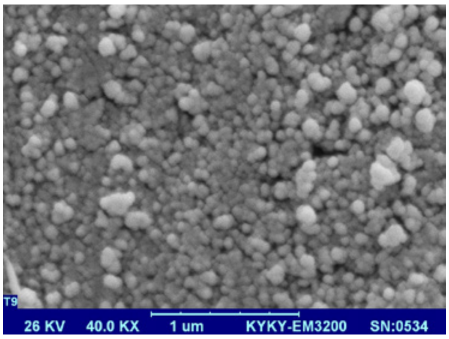

Fig. 11. SEM image of sample T9

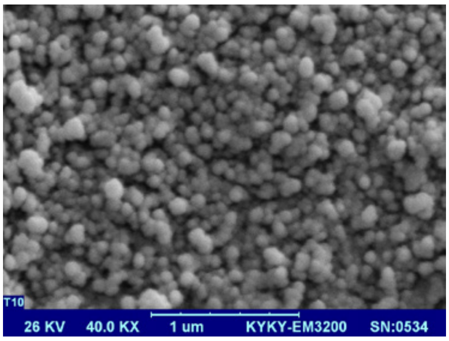

Fig. 12. SEM image of sample T10

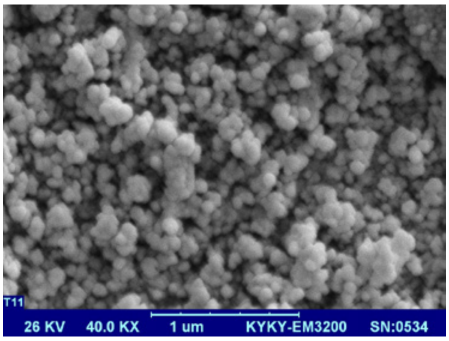

Fig. 13. SEM image of sample T11

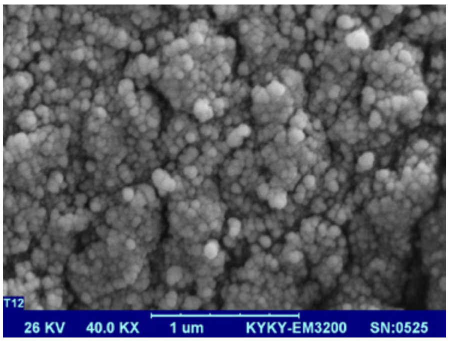

Fig. 14. SEM image of sample T12

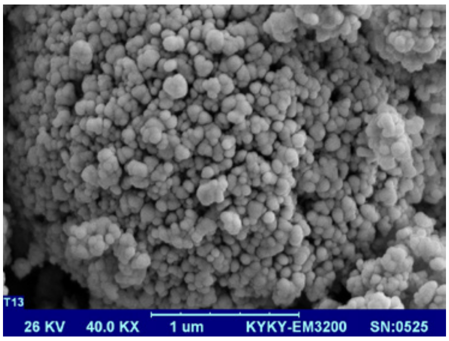

Fig. 15. SEM image of sample T13

of the sample T9 after sonication is illustrated in Fig. 16. The average particles' size measured from TEM was 40 nm, in relative harmony with SEM image (Fig. 11). It is evident that particles were shaped irregularly and specific morphology could not be observed.

Analysis of the experimental data and optimization

The signal to noise ratio (S/N) approach was used for analysis of particle size data. Since the target of the study is synthesis of silver nanoparticles with smallest sizes, the corresponding S/N ratio calculation was done by "smaller is better" strategy of Taguchi method.

$$\frac{S}{N} = -\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n} y_i^2\right) \qquad (1)$$

y_i= result in i-th experiment

The mean S/N ratios of results in each level of relative parameters are illustrated in Table 4. The highest value of the mean S/N ratio for a parameter was considered as optimum level of relative parameter [23]. The optimum result of particles

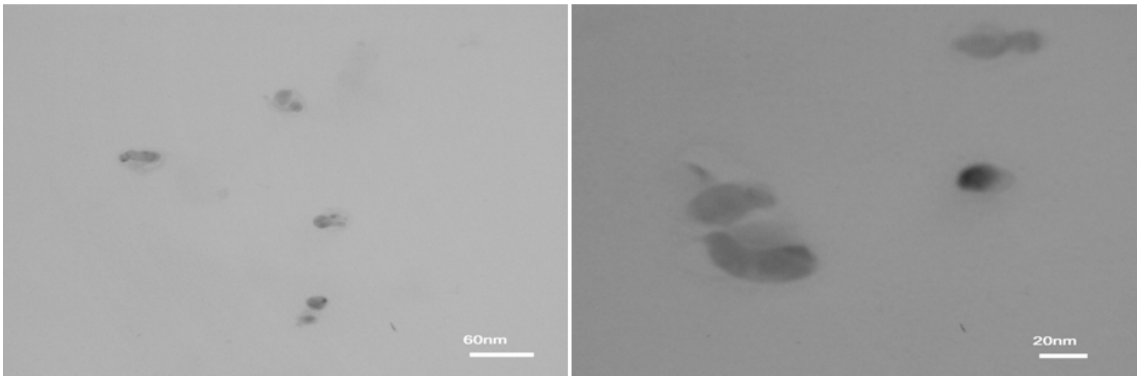

Fig. 16. TEM images of sample T9 at two magnifications

Table 4. Mean S/N ratio of results

Level	MAM (g)	MBAM/MAM	$AgNO_3$/MAM	Duration of calcination (h)	Temperature of calcination (□C)
1	-37.34	-35.84	-37.05	-37.18	-35.96
2	-36.59	-37.12	-36.55	-37.08	-36.60
3	-35.08	-36.91	-35.51	-35.91	-36.91
4	-36.31	-35.44	-36.2	-35.15	-35.84
Delta	2.25	1.68	1.54	2.04	1.07
Rank	1	3	4	2	5

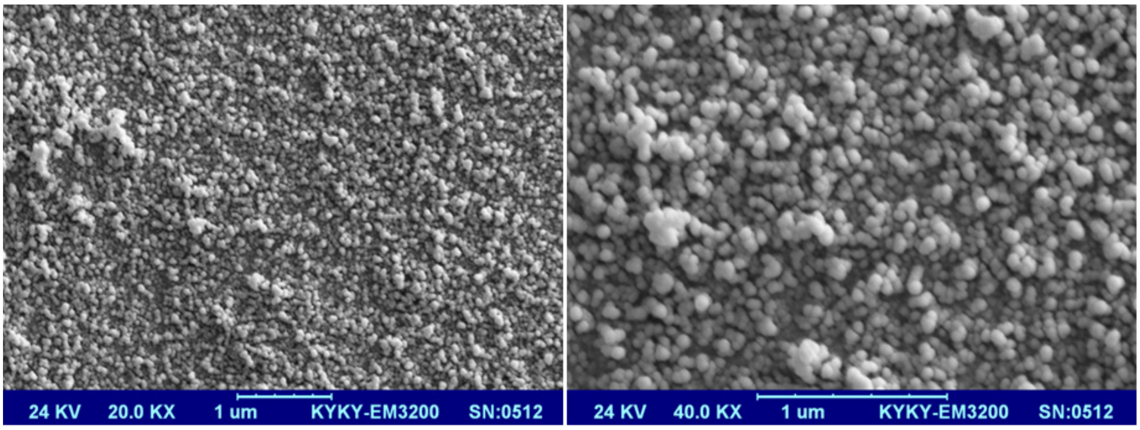

Fig. 17. SEM images of sample synthesized in optimum levels at two magnifications

size was achieved with levels A3B4C3D4E4. So the optimum value of MAM, MBAM/MAM, $AgNO_3$/MAM, duration and temperature of calcination were 4.25 g, 1:3, 1:15, 6 h and 650°C, respectively.

Taguchi method introduces a correlation for prediction of the results with a desired level of each parameter. The predicted S/N ratio using the optimum level of parameters is calculated by the following equation.

$$(\frac{S}{N})_p = (\frac{S}{N})_m + \sum_{i=1}^{n}((\frac{S}{N})_i - \left(\frac{S}{N})_m\right) \quad (2)$$

Where $(S/N)_m$ is the average of S/N ratio calculated from Table 3 and is −36.33, $(S/N)_i$ is the mean S/N ratio at the optimum level, and n is the number of the parameters that their effects are investigated. From Table 4, the $(S/N)_i$ is −35.08, −35.44, −35.51, −35.15, −35.84 for A3, B4, C3, D4, E4, respectively. Thus the predicted S/N ratio is -31.71 and relative predicted size is 32 nm.

Finally, an evaluation experiment was done and a sample with the optimum level of parameters was synthesized. SEM of the synthesized nanosilver from the evaluation test is illustrated

Table 5. Evaluation test with optimum levels

	Level	Particle size	S/N ratio
Prediction	A3B4C3D4E4	32	-31.71
Experiments	A3B4C3D4E4	34	-30.63

in Fig. 17 and measured particle size was 34 nm. Table 5 shows the average size of particles obtained in evaluation experiment and the size predicted by Taguchi method. Suitable agreement exists between the predicted result and the experimental measurement.

Table 4 demonstrates the difference between maximum and minimum of S/N ratio, and it shows that the monomer content has the main effect on the particle size. It seems that increasing the monomer content, the size of void spaces in the polymeric gel reduces by resulting in a reduction of the product size. Effectiveness of duration of calcination, cross linker to monomer ratio, silver salt to monomer ratio and temperature of calcination are ranked from 2 to 5, respectively.

CONCLUSION

In summary, high purity silver nanoparticles were successfully synthesized by gelcasting method and washing. Gelcasting is a simple and reliable method for synthesis of silver nanoparticles. By adjusting the effective parameter, preparation of small particles is possible. The monomer content is the most effective parameter on the product's particles size and duration of calcination, cross-linker to monomer ratio, silver salt to monomer ratio and temperature of calcination are ranked from 2 to 5, respectively. Synthesized nano-powder can be used in gas hydrate for promoting the kinetic of formation. Future work will concentrate on kinetic study of methane hydrate in presence of the synthesized nanoparticles.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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