Chemical Engineering Journal 104 (2004) 55–61

Chemical Engineering Journal

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Optimization of experimental conditions based on the Taguchi robust design for the formation of nano-sized silver particles by chemical reduction method

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Received 5 June 2004; received in revised form 7 August 2004; accepted 19 August 2004

Abstract

Taguchi robust design method with L_9 orthogonal array was implemented to optimize experimental conditions for the preparation of nano-sized silver particles using chemical reduction method. Particle size and the particle size distribution of silver nano-particles were considered as the properties. Molar concentration ratio of *R* ([$AgNO_3$]/[reducing agent (hydrazine)]) value, concentration of dispersant (sodium dodecyle sulfate, SDS), and feed rate of reactant were chosen as main parameters. As a result of Taguchi analysis in this study, the concentration of dispersant was the most influencing parameter on the particle size and the size distribution. The feed rate of reactant had also principal effect on particle size distribution. The optimal conditions were determined by using Taguchi robust design method and nano-sized silver particles (∼8 nm) were synthesized. In addition, by the analyses of X-ray diffraction, high-resolution transmission electron microscopy, and electron diffraction (ED) pattern, the resultant particles were characterized to be pure crystalline silver with a face-centered cubic (fcc) structure.

Keywords: Silver nano-particles; Chemical reduction method; Taguchi robust design; Optimization

1. Introduction

Ultrafine metal and metal alloy powders have many important applications in electronics, dental, and chemical industries [1,2]. Of these metal powders, nano-sized Ag particles have been widely used in the electronics industry for the manufacture of conductive thick film circuits and for the internal electrodes of multilayer ceramic capacitors [3,4]. Especially, silver nano-particles with narrow particle size distribution are of considerable current use in chemical industry and medicine due to unique properties such as thermal conductivity, high resistance to oxidation, and bactericidal action. Therefore, many efforts have sought to produce silver nano-particles with controlled particle size, shape, and particle size distribution.

Several methods currently have been applied to synthesize silver nano-particles, such as physical processes of atomization or milling [5], chemical methods of thermal decomposition, chemical reduction [6], sol–gel [7], water-in-oil (W/O) microemulsions [8,9], or electrochemical processes [10–12]. Of those chemical methods, the W/O microemulsion approach is a method to prepare nanometer-sized Ag, ZrO_2, and $BaTiO_3$ particles. W/O microemulsion system, which consists of an oil phase, a surfactant phase, and an aqueous phase, is a thermodynamically stable isotropic dispersion of the aqueous phase in the continuous oil phase. In addition to the W/O microemulsions, the method of chemical reduction from aqueous solutions is also most preferable for obtaining nano-sized particles of silver, while the conventional processes usually produce powders with micron size, and irregular shape and aggregation. The essential

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doi:10.1016/j.cej.2004.08.003

feature of this chemical reduction method is to give a desirable particle shape and size at high yield and low preparation costs.

In the formation of silver nano-particles by chemical reduction method, there are several factors that are important to prepare nano-sized powder of silver. Properties of silver nano-particles obtained by chemical reduction method are affected by various parameters such as the molar concentration ratio of R ([$AgNO_3$]/[reducing agent]) value, dispersant concentration, and feed rate of reactant. The interrelationships between the above parameters are complex, and the analysis of this chemical reduction system to optimize the factors is a time and labor-consuming work. Hence, the analyses using conventional experimental methods are inefficient.

Therefore, Taguchi robust design method [13–15] was introduced in this paper. Taguchi method is a combination of mathematical and statistical techniques used in an empirical study. It is economical for characterizing a complicated process. It uses fewer experiments required in order to study all levels of all input parameters, and filters out some effects due to statistical variation. Taguchi method can also determine the experimental condition having the least variability as the optimum condition. The variability of a property is due to 'noise factor', which is a factor difficult to control. On the contrary, the factor easy to control is called 'control factor'. The variability can be expressed by signal to noise (S/N) ratio [15]. The experimental condition having the maximum S/N ratio is considered as the optimal condition, as the variability of characteristics is in inverse proportion to the S/N ratio.

The objectives of this work are: (1) to suggest a method for the synthesis of silver nano-particles by using a chemical reduction process, (2) to apply the Taguchi robust design method on the optimization of properties and to obtain the silver nano-particles with narrow particle size distribution by using optimal synthesis conditions, and (3) to evaluate the effect of several parameters on the particle size and the size distribution of silver nano-particles.

2. Experimental procedure

2.1. Starting materials

Silver nano-particles were prepared by chemical reduction method by adding of silver nitrate ($AgNO_3$ (99.99%), Aldrich) aqueous solutions to beaker consisting of hydrazine hydrate ($N_2H_4{\cdot}H_2O$ (98%), Aldrich) and sodium dodecyle sulfate (SDS) ($CH_3(CH_2)_{11}OSO_3Na$ (99%), Aldrich) aqueous solution. All chemicals were reagent grade. In this work, hydrazine hydrate and sodium dodecyle sulfate were used as a reducing agent and a dispersant, respectively. In addition, acetone (99%, Duksan) was used as a washing agent and water used in this experiment was double distilled and deionized. The solutions were prepared in a glove box at room temperature under dry air. The humidity in the glove box was kept below a few percent.

2.2. Preparation and characterization of silver nano-particles

The experimental investigation was carried out at room temperature and under atmospheric pressure using silver nitrate solution as the precursor. The solution of chemical reduction system was prepared by dissolving hydrazine hydrate and sodium dodecyle sulfate in distilled water and by adding a required amount of distilled water with $AgNO_3$. In this work, the molar concentration ratio of R ([$AgNO_3$]/[hydrazine]) was varied in the range of 1–7, and the concentration of hydrazine hydrate was fixed at 0.005 M. In addition, the concentrations of SDS dispersant and feed rate of $AgNO_3$ aqueous solution were changed in the range of 0.001–0.01 M and 1.3–15.9 ml/min, respectively.

The apparatus consists of a reservoir of starting solutions, a microfeed pump to supply the solutions, a water bath, and a reactor with stirrer. The microfeed pump (MP-3, EYELA) with a constant feed rate fed the starting solution A ($AgNO_3/H_2O$) into the reactor with another solution B (hydrazine/SDS/H_2O) and the experiment was conducted with dry nitrogen. The reaction was initiated by adding the solution A into the solution B with stirring for 10 min. The feed rate of $AgNO_3$ aqueous solution was controlled by a microfeed pump. The semi-batch system using this microfeed pump is easier than a batch system in controlling the size, shape, and size distribution because of its short nucleation and a slow reaction rate. The silver nano-particles precipitated were separated in a centrifuge at 10,000 rpm for 10 min and were then washed with acetone to remove organics from the particles. The particles were dried at 70 °C for 24 h. A schematic diagram of the experimental procedure is depicted in Fig. 1.

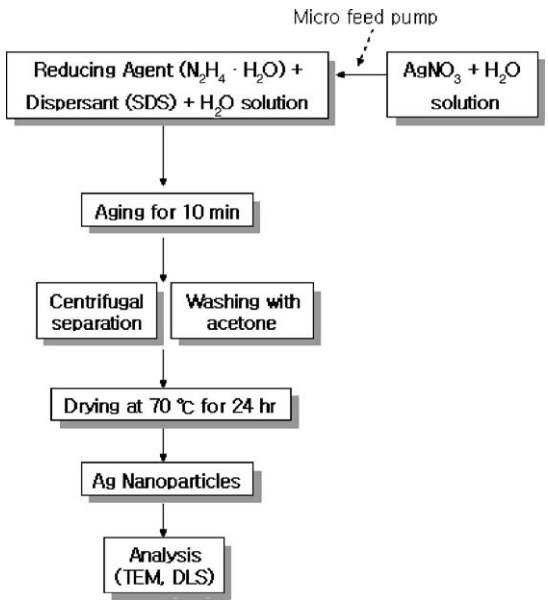

Fig. 1. Experimental procedure for the synthesis of silver nano-particles using chemical reduction method.

Table 1
Parameters and levels used in this experiment

		Levels		
		Low (1)	Medium (2)	High (3)
A	Molar concentration ratio of R ([$AgNO_3$]/[hydrazine]) value (−)	1	4	7
B	Dispersant concentration (M)	0.001	0.005	0.01
C	Feed rate (ml/min)	1.3	5.9	15.9

The particle size and the size distribution of silver nano-particles were observed using field emission scanning electron microscope (FE-SEM, JEOL, JSM-6330F, Japan), transmission electron microscope (TEM, JEOL, JEM-2020, Japan), and a dynamic light scattering (LPA-3000, 3100, Otsuka electronics). The dried silver nano-particles were subjected to UV–vis spectrophotometer (Agilent 8453, Hewlett–Packard, USA) and zeta potential analyzer (LEZA-600, Otsuka electronics, Japan) to determine the particle size distribution and colloidal stability, respectively. In addition, the major phase of the obtained particles was analyzed by X-ray diffraction (D/MAX 2000, Rigaku, Japan) using Cu Kα radiation.

2.3. Orthogonal array and experimental parameters

Taguchi's orthogonal array table [16,17] was used by choosing three parameters that could affect the particle size and standard deviation. Table 1 shows the parameters and levels used in this experiment. The orthogonal array of L_9 type was used and is represented in Table 2. L and subscript 9 mean Latin square and the repetition number of the experiment, respectively. Four three-level parameters can be positioned in a L_9 orthogonal array table. One column of the orthogonal array was assigned as error term to increase the accuracy of the analyses. The numbers 1, 2, and 3 in Table 2 indicate the first, second, and third levels of a factor, respectively.

3. Results and discussion

3.1. Determination of optimal conditions using Taguchi robust design

A Taguchi robust design method was used to identify the optimal conditions and to select the parameters having the most principal influence on the particle size and the size distribution of silver nano-particles. The structure of Taguchi's orthogonal robust design and the results of measurement are shown in Table 2 and the smallest values of particle size (10.4 nm) and standard deviation (±1.0 nm) are shown in experiment no. 3. These values mean that silver nano-particles having an average size of 10.4 nm are synthesized and the highly monodispersed nano-particles with the range of 9.4–11.4 nm are obtained. In the Taguchi method, the terms 'signal' and 'noise' represent the desirable and undesirable values for the output characteristic, respectively. Taguchi method uses the S/N ratio to measure the quality characteristic deviating from the desired value. The S/N ratios are different according to the type of characteristic. In the case that smaller characteristics are better, the S/N ratio is defined as [14]:

$$\frac{\mathrm{S}}{\mathrm{N}}\ \text{ratio}\,[\mathrm{dB}] = -10\log\left[\frac{y_1^2 + y_2^2 + y_3^2 + \ldots}{n}\right] \quad (1)$$

where y_i is the characteristic property, n is the replication number of the experiment. The unit of S/N ratio is decibel (dB), which is frequently used in communication engineering. Consistent with its application in engineering and science, the value of S/N is intended to be large; hence, the value of $(y_1^2 + y_2^2 + y_3^2 + \ldots)/n$ should be small. To obtain optimal conditions, the-lower-the-better quality characteristic for particle size and standard deviation must be taken.

Table 2 shows the S/N ratio for particle size and standard deviation using Eq. (1). Since the experimental design is orthogonal, it is then possible to separate out the effect of each parameter at different levels. For example, the mean S/N ratio for the R value at levels 1, 2, and 3 can be calculated by averaging the S/N ratios for the experiments 1–3, 4–6, and 7–9, respectively. The mean S/N ratio for each

Table 2
Experimental measured values for particle size and standard deviation (S.D.) of silver particles and S/N ratio (Taguchi orthogonal array table of $L_9(3^4)$)

Experiment no.	A	B	C	Error	Average particle size		Standard deviation	
					Raw data (nm)	S/N ratio (dB)	Raw data (±nm)	S/N ratio (dB)
1	1	1	1	1	62.6	−35.93	15	−23.52
2	1	2	2	2	22.0	−26.85	3	−9.54
3	1	3	3	3	10.4	−20.34	1	0.0
4	2	1	2	3	34.3	−30.71	5	−13.98
5	2	2	3	1	67.2	−36.55	14	−22.92
6	2	3	1	2	26.7	−28.53	3	−9.54
7	3	1	3	2	54.3	−34.69	12	−21.58
8	3	2	1	3	24.5	−27.78	23	−27.24
9	3	3	2	1	14.0	−22.92	2	−6.02

Table 3
S/N response table for particle size

Symbol	Parameter	Mean S/N ratio (dB)			
		Level 1	Level 2	Level 3	Maximum–minimum
A	R ([$AgNO_3$]/[hydrazine]) value	−27.71	−31.93	−28.47	4.22
B	Dispersant concentration (M)	−33.78	−30.39	−23.93	9.85
C	Feed rate (ml/min)	−30.75	−26.83	−30.53	3.92

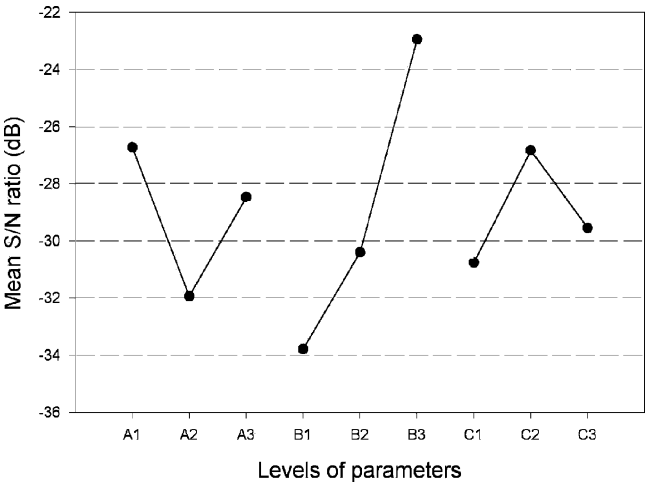

Fig. 2. S/N graph for particle size.

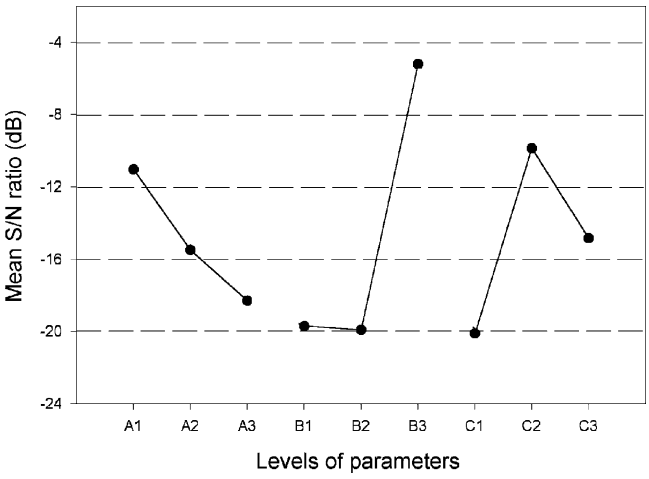

Fig. 3. S/N graph for standard deviation.

level of the other parameters can be computed in the similar manner.

The mean S/N ratio for each level of the parameters is summarized and the S/N response table for particle size is shown in Table 3. As shown in Table 3, the maximum–minimum values of dispersant (SDS) concentration are the highest values. Therefore, it can be found that dispersant (SDS) concentration is the significant parameter for affecting particle size. Fig. 2 shows the S/N response graph for particle size. As shown in Eq. (1), the greater the S/N ratio, the smaller is the variance of particle size around the desired value. Therefore, the optimum condition is A1, B3, and C2. In other words, based on the S/N ratio, the optimal parameters (conditions) for particle size are A at level 1, B at level 3, and C at level 2.

The S/N response table and graph for standard deviation are shown in Table 4 and Fig. 3, respectively. In the case of standard deviation, the optimal conditions are A1, B3, and C2. It was also found that the values (maximum–minimum) of B (dispersant concentration) and C (feed rate) are higher than any other factors, implying that these parameters have the most significant influence. Consequently, the particle size and the size distribution of silver nano-particles were all mainly affected by the concentration of SDS dispersant. Fig. 4 shows the FE-SEM micrographs of silver powders according to the concentration of SDS dispersant, which is the most principal parameter. The particle size decreased from sub-micron size to nanometer size with increasing of the SDS concentration. The reason for these results can be explained as follows: in general, the mechanism of stabilization for maintaining colloidal dispersion is divided into five ways [18], in other words, (1) electrostatic stabilization, (2) steric stabilization, (3) stabilization by hydration forces, (4) depletion stabilization, and (5) stabilization by van der Waals force. In the case of inorganic particle's colloidal system, it has been known that stabilization of the system is resulted from electrostatic repulsive force and van der Waals force. In the case of polymer materials such as SDS adsorbed on the surface of colloidal particles, however, the stabilization of colloid is determined

Table 4
S/N response table for standard deviation

Symbol	Parameter	Mean S/N ratio (dB)			
		Level 1	Level 2	Level 3	Maximum–minimum
A	R ([$AgNO_3$]/[hydrazine]) value	−11.02	−15.48	−18.28	7.26
B	Dispersant concentration (M)	−19.69	−19.90	−5.19	14.71
C	Feed rate (ml/min)	−20.10	−9.85	−14.84	10.25

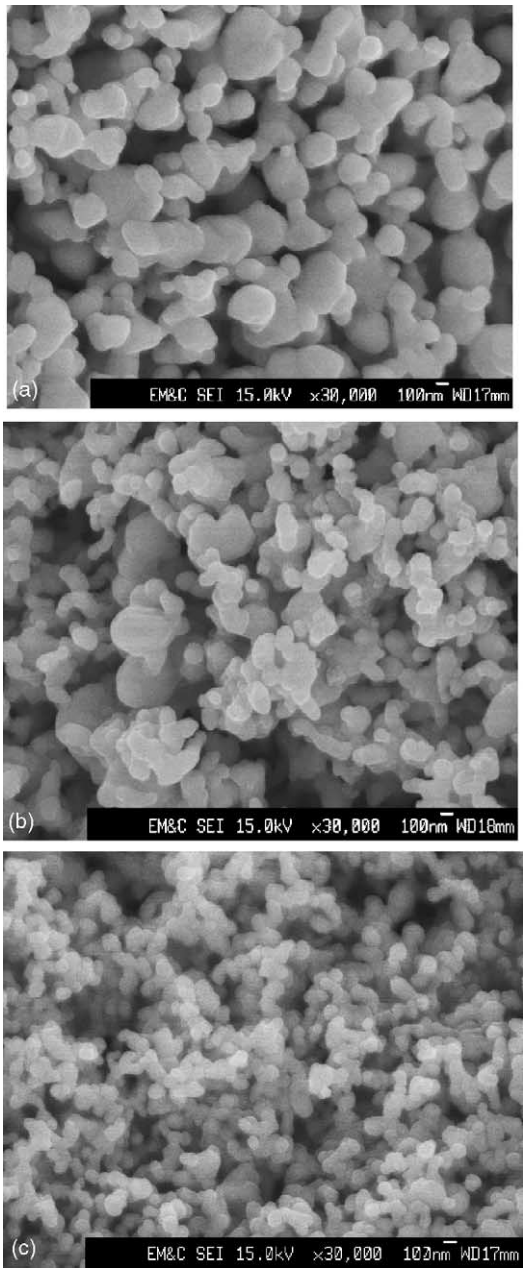

Fig. 4. FE-SEM micrographs of silver powders according to the concentration of SDS: (a) 0.001 M, (b) 0.005 M, and (c) 0.01 M (R = 4, feed rate: 5.9 ml/min).

by more complicated mechanisms. In other words, the particles are stabilized by some reaction of the above mechanisms, surface property of the particles, and improvement of particle's surface by adsorbed polymers. Therefore, it is assumed that colloidal system using water-soluble polymer such as SDS is stabilized and well dispersed by mechanisms of (1), (2), and (3).

Once the optimal level of the design parameters has been selected, the final step is to predict and verify the improvement of the quality characteristic using the optimal level of the design parameters. The predicted S/N ratio using the optimal level of the design parameters can be calculated as [13]:

$$\left[\frac{S}{N}\right]_{\text{predicted}} = \left[\frac{S}{N}\right]_{m} + \sum_{i=1}^{n}\left(\left[\frac{S}{N}\right]_{i} - \left[\frac{S}{N}\right]_{m}\right) \quad (2)$$

where $[S/N]_m$ is the total mean S/N ratio, $[S/N]_i$ is the mean S/N ratio at the optimal level, and n is the number of the main design parameters that affect the quality characteristic. In the case of particle size, the value of $[S/N]_m$ calculated from Table 2 is −29.37. Also, $[S/N]_i$ for A1, B3, and C2 can be obtained from Table 3 and the values are −27.71, −23.93, and −26.83, respectively. By using these values, Eq. (2) can be written as $[S/N]_{\text{predicted}} = -29.37 + [(-27.71 + 29.37) + (-23.93 + 29.37) + (-26.83 + 29.37)]$. Therefore, the predicted S/N ratio (−19.7) for particle size can then be obtained and the corresponding estimated particle size can also be calculated by using Eq. (1). In other words, the value of S/N ratio (−19.7) at optimal condition (A1B3C2) is substituted into Eq. (1), and then Eq. (1) can be expressed as $-19.7 = -10\log(y^2)$. Finally, estimated particle size (9.6 nm) can be obtained. The predicted S/N ratio for standard deviation can also be computed by same procedure.

Table 5 shows the comparison of the predicted particle size and standard deviation with the experimental results using the optimal conditions. There is good agreement between the predicted and experimental particle size being observed. The increase of the S/N ratio from no. 3 (−20.34) as shown in Table 2 to the optimal actual data (−17.50) is 2.84 dB, which means that the particle size is decreased by about 0.72 times. The comparison of the predicted standard deviation with the experimental data is also shown in Table 5, where a predicted standard deviation roughly consistent with the actual results is noted. Consequently, particle size and standard deviation in the synthesis of silver nano-particles can be decreased and improved through the Taguchi method approach.

3.2. Characterization of silver nano-particles

The TEM micrograph and particle size distribution of the silver nano-particles obtained at optimal conditions of Table 5 are shown in Fig. 5. The silver nano-particles with a particle size of 8 nm were prepared, as shown in Fig. 5(a). The particle

Table 5
Results of the confirmation experiment for particle size and standard deviation

	Average particle size (nm)			Standard deviation (±nm)		
	Level	Particle size (nm)	S/N ratio (dB)	Level	Standard deviation (nm)	S/N ratio (dB)
Prediction	A1B3C2	9.6	−19.7	A1B3C2	±0.7	3.8
Experiment	A1B3C2	7.5	−17.5	A1B3C2	±1.0	0.0

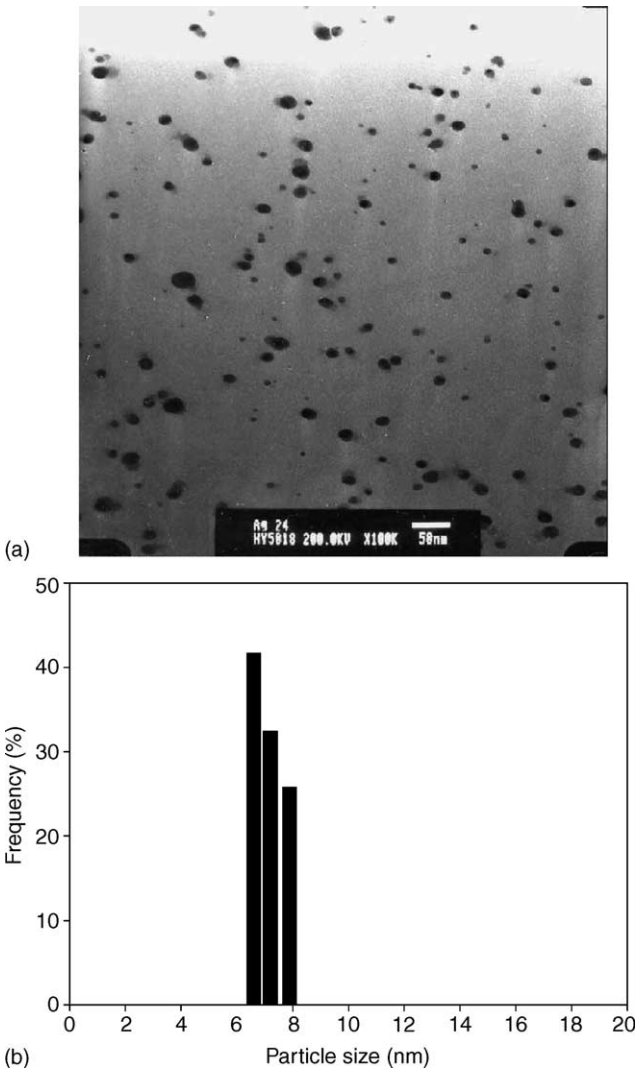

Fig. 5. TEM photograph (a) and particle size distribution (b) of the silver nano-particles obtained at optimal conditions.

size distribution of the powder was also measured with a laser particle size analyzer and it can be found that monodispersed silver nano-particles were prepared (Fig. 5(b)). These results can be also verified in Fig. 6.

Fig. 6 demonstrates the UV absorption spectrum of silver nano-particles obtained from optimal conditions. In general, it was known that silver nano-particles have a strong absorption peak at about 400–450 nm [19]. This UV absorption peak means the confirmation of nano-sized silver particles, particle size, and the particle size distribution. The narrower the absorption peak is, the smaller and better particle size and standard deviation are, respectively. Therefore, whether the formation of nano-sized silver particles with narrow size distribution is accomplished or not can be predicted by analysis of UV absorption peak. This result is identical to that of Fig. 5.

Typical X-ray diffraction pattern and electron diffraction (ED) pattern of Ag nano-particles prepared at optimal conditions are given in Fig. 7. XRD analysis shown in Fig. 7(a) indicated that the silver nano-particles are crystallized show-

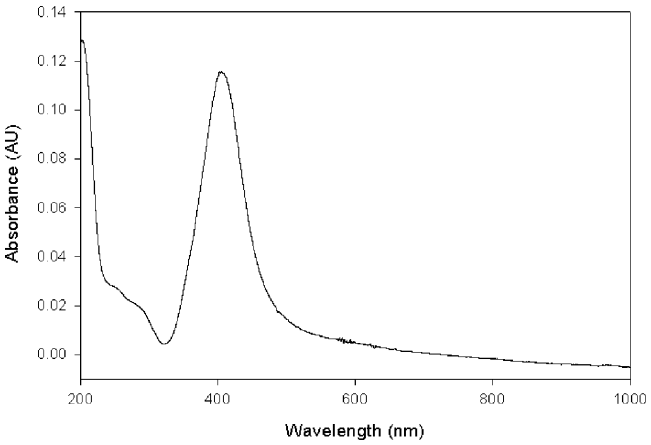

Fig. 6. A typical UV absorption spectrum of silver colloidal solution.

ing peaks of (1 1 1), (2 0 0), and (2 2 0). This revealed that the resultant particles were pure face-centered cubic (fcc) silver [20]. The corresponding electron diffraction pattern of silver nano-particles is shown in Fig. 7(b). Three fringe patterns can be observed and they are related to the (1 1 1), (2 0 0), and (2 2 0) planes of pure fcc silver.

Fig. 8 depicts the effect of pH on zeta potential and particle size of silver nano-particles prepared at optimal conditions. The minus value of zeta potential is shown in overall pH area

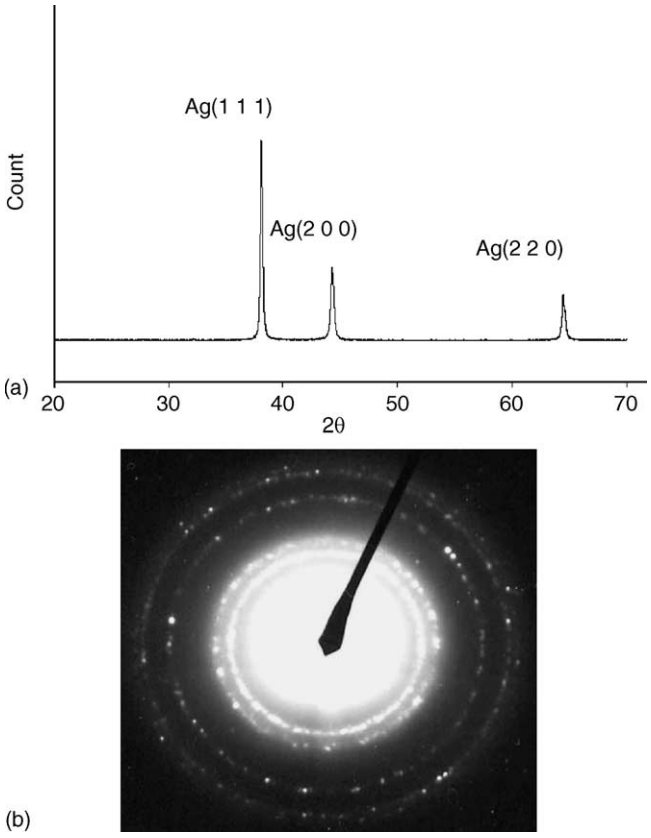

Fig. 7. XRD pattern (a) and electron diffraction pattern (b) of silver nano-particles obtained at optimal conditions.

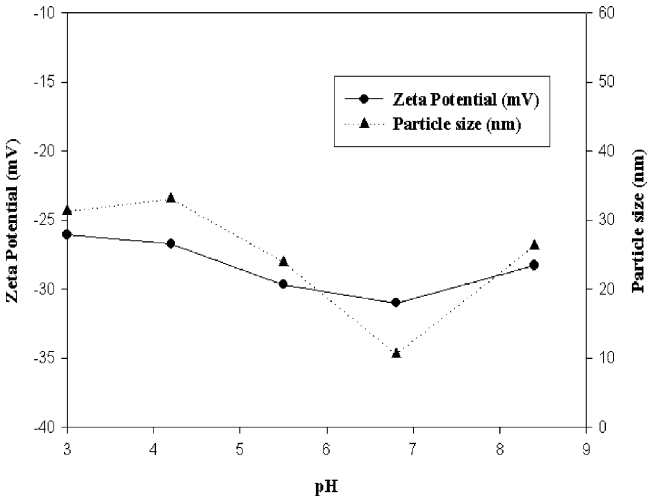

Fig. 8. Effect of pH on zeta potential and particle size of silver nano-particles prepared at optimal conditions.

and it is thought that these results are affected by dispersant (SDS) as an anion surfactant. In addition, the absolute values of zeta potential are within the limits of 25–35 mV, which means that silver nano-particle colloids have a narrow particle size distribution [21]. The particle size and stability of the silver nano-particle colloids are also influenced by the pH of solutions. As the absolute value of zeta potential increased, the stability was higher and the particle size of the colloidal particles decreased. Consequently, the zeta potential of the colloidal particles was affected by the pH of the solution, and the optimal pH for the most stable colloid formation was about 6–7 in the experimental conditions.

4. Conclusions

Nano-sized silver particles were synthesized by chemical reduction method in this work. Taguchi robust design method was used to optimize the parameter values for obtaining desired characteristics. Various factors affecting the particle size and standard deviation were analyzed and optimized. As a result, the concentration of SDS dispersant was the main parameter having significant effects on particle size and the particle size distribution of silver nano-particles. By optimal conditions of this method, silver nano-particles (~8 nm) with narrow particle size distribution were prepared and these results were in good agreement with data analyzed by Taguchi robust design method. The results of UV-absorption spectrum and zeta potential showed that the nano-sized silver particles were prepared at optimal conditions. In addition, it can be also found that the resultant particles were pure face-centered cubic silver from XRD analysis.

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