Preparation of colloidal silver nanoparticles by chemical reduction method

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Abstract−Colloidal silver nanoparticles were obtained by chemical reduction of silver nitrate in water with sodium borohydride ($NaBH_4$) in the presence of sodium dodecyl sulfate (SDS) as a stabilizer. The obtained nanoparticles were characterized by their UV-vis absorption spectra and transmission electron micrograph (TEM) images. The UV-vis absorption spectra showed that $NaBH_4$ served not only as a reducing agent but also as a stabilizer, which protects the aggregation of silver nanoparticles. The TEM images showed that the particles were dispersed better with increasing the $NaBH_4$ concentration.

Key words: Silver Nanoparticles, Chemical Reduction, SDS, UV-vis Absorption Spectra, TEM

INTRODUCTION

During the past few decades, silver nanoparticles have attracted considerable interest from the chemical industry and medicine due to unique properties, such as high thermal conductivity, high resistance of oxidation, and antibacterial activity [1-5]. Recently, various inorganic antibacterial materials containing silver have been developed and some are in commercial use [6]. The antibacterial activity of silver nanoparticles is influenced by the size of the particles, contrary to bactericide effects of ionic silver [7]. Thus, silver nanoparticles with small size and without aggregation between particles are preferable in this application. Many methods, including a chemical reduction method [8], a polyol method [9] and a radiolytic process [10], have been developed for the synthesis of silver nanoparticles. Among these methods, the chemical reduction method has been widely studied, due to its advantages of yielding nanoparticles without aggregation, high yield and low preparation cost [11].

The chemical reduction method involves the reduction of $AgNO_3$ by a reducing agent in the presence of a suitable stabilizer, which is necessary in protecting the growth of silver particles through aggregation. In the formation of silver nanoparticles by the chemical reduction method, the particle size and aggregation state of silver nanoparticles are affected by various parameters, such as initial $AgNO_3$ concentrations, reducing agent/$AgNO_3$ molar ratios, and stabilizer concentrations.

It is known that in the case of silver nanoparticles, the UV-vis absorption spectra are very sensitive to the particle size and their aggregation state, since the silver nanoparticles strongly absorb in the visible region due to surface plasmon resonance [12-14]. In this study, the particle size and degree of aggregation of silver nanoparticles, were investigated by UV-vis absorption spectra, prepared by varying the experimental parameters of initial $AgNO_3$ concentrations, reducing agent/$AgNO_3$ molar ratios, and stabilizer concentrations.

EXPERIMENTAL

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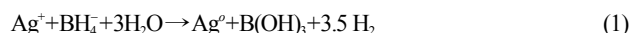E-mail: bslee@kier.re.kr

Silver nitrate ($AgNO_3$, 99.5%) purchased from Junsei Chemicals was used as the precursor to prepare silver nanoparticles. Sodium borohydride ($NaBH_4$, 98%) and sodium dodecyl sulfate (SDS, 98%) purchased from Aldrich Chemicals were used as the reducing agent and stabilizer for the silver nanoparticles, respectively. $AgNO_3$ solution was prepared by dissolving the required amount of $AgNO_3$ in 50 ml distilled water. Separately, the $NaBH_4$ solution was prepared by dissolving $NaBH_4$ and SDS in 50 ml distilled water for half an hour together. Silver nanoparticles were produced by dropping the $AgNO_3$ solution into the $NaBH_4$ solution with SDS slowly. After all solutions were added, the mixed solutions were stirred for 1 hour more.

The aggregation state of particles was observed with a UV-vis spectrometer (UV-2450, Shimadzu, Japan). The particle size and aggregation state of particles were further measured with transmission electron micrograph (TEM, Jeol, JEM-1010, Japan) at 80 kV accelerating voltage.

RESULTS AND DISCUSSION

1. Effect of Initial $AgNO_3$ Concentration

To prepare the stable silver nanoparticles via the chemical reduction method, it is important to choose appropriate stabilizer and reducing agent. In this work, a water soluble stabilizer SDS and a strong reducing agent $NaBH_4$ were used. Silver nitrate is reduced by sodium borohydride in the presence of stabilizer (SDS), resulting in silver nanoparticles, according to the following Eq. (1) [15].

$$Ag^+ + BH_4^- + 3H_2O \rightarrow Ag^o + B(OH)_3 + 3.5\,H_2 \tag{1}$$

In the formation of silver nanoparticles by the chemical reduction method, the order of reactant addition, dropping silver nitrate solution into $NaBH_4$ solution with stabilizer, is important to obtain stable silver nanoparticles [16]. The reverse order of reactant addition causes the immediate precipitation of silver nanoparticles. Fig. 1 shows the UV-vis spectra of colloidal silver nanoparticles prepared with different initial $AgNO_3$ concentrations (0.0001 M, 0.0002 M, 0.0005 M and 0.001 M). The nanoparticles were synthesized at the conditions of $NaBH_4$/$AgNO_3$ molar ratio of 10 and SDS/$AgNO_3$ weight
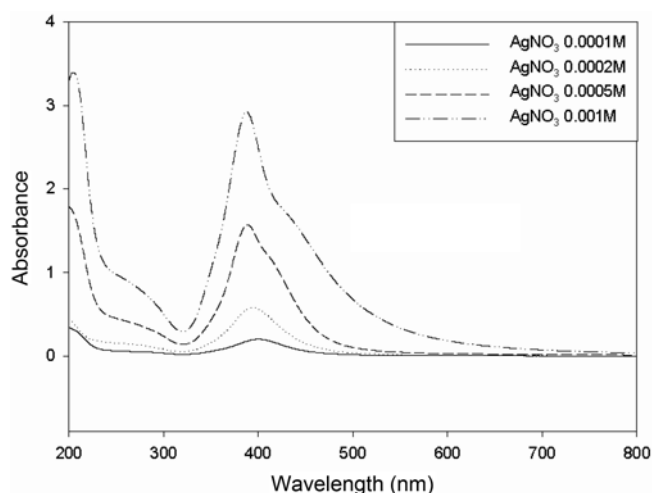
Fig. 1. UV/vis absorption spectra of the silver nanoparticles prepared via reduction of AgNO₃ with different initial concentrations.

ratio of 2. The color of the solutions depended on the concentration of added AgNO₃ solutions. With increasing the initial AgNO₃ concentration, the color of solution changed from yellow to brown. The absorption peak at around 400 nm in Fig. 1 is attributed to the surface plasmon excitation of silver nanospheres, indicating the formation of silver nanoparticles [17]. At low AgNO₃ concentrations (0.0001 M, 0.0002 M), a weak absorption maximum of surface plasmon peaks was observed at 400 nm, showing that silver nanoparticles were produced at a relatively low concentration. With increasing the AgNO₃ concentration, the intensity of the maximum plasmon peak increased, indicating that higher concentrations of silver nanoparticles were formed.

2. Effect of NaBH₄ Concentrations

To understand the role of NaBH₄ concentrations, the reduction reaction was carried out by varying molar ratios of NaBH₄/AgNO₃ (0.5-15) at the conditions of initial AgNO₃ concentration (0.001 M)

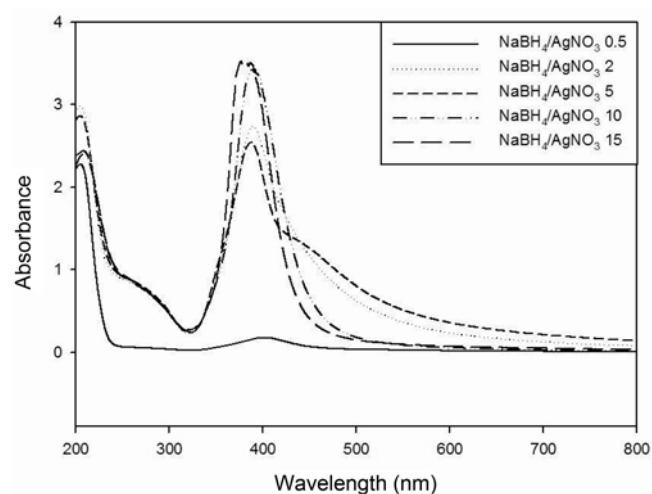and SDS/AgNO₃ weight ratio of 2. UV-vis spectra of different molar ratios of NaBH₄/AgNO₃ are shown in Fig. 2. When small molar ratio of NaBH₄/AgNO₃ (0.5) was used, a weak plasmon peak centered at 400 nm was observed, indicating that silver nanoparticles of a relatively low concentration were produced, due to insufficient reduction reaction. It is well known that the UV-vis absorption peak can give information on the degree of dispersion of silver nanoparticles [11]. The narrower the absorption peak, the better the degree of dispersion of nanoparticles. In the NaBH₄/AgNO₃ molar ratios of 2 and 5 the intensity of the absorption peak at 400 nm increased, and the absorption peak became broad, indicating the aggregation of silver nanoparticles. However, when the NaBH₄/AgNO₃ molar ratios were 10 and 15, narrow absorption peaks were obtained, suggesting that the silver nanoparticles were well dispersed. These results are well consistent with Liu et al. [17]. According to them, a small amount of NaBH₄ was used; the boron hydroxide produced through hydrolysis of NaBH₄ by the above Eq. (1) was absorbed to the silver nanoparticles, reducing the electron density of surfaces and causing profound aggregation of silver nanoparticles. On the other hand, when excess amount of NaBH₄ was used, thick BH₄⁻ layer prevented the boron hydroxide from absorbing to the surfaces of silver nanoparticles, resulting in well-dispersed nanoparticles. These results indicate that NaBH₄ served not only as a reducing agent but also as a stabilizer, which protects the aggregation of silver nanoparticles.

Fig. 3 shows the TEM images of silver nanoparticles prepared with different NaBH₄/AgNO₃ molar ratios (2, 10). With increasing the NaBH₄ concentrations, the particle size had no obvious changes (the particle diameter ranges from 30 to 40 nm). However, the aggregation state of nanoparticles depended on different NaBH₄/AgNO₃ molar ratios. When NaBH₄/AgNO₃=2, profound aggregation of silver nanoparticles was observed in Fig. 3(a). On the other hand, in the case of NaBH₄/AgNO₃=10 in Fig. 3(b), the aggregation was reduced, and the dispersion became far better. These results are well consistent with the UV-vis spectra in Fig. 2.

3. Effect of SDS Concentrations

The main purpose of introducing SDS to the solution was to prevent the silver nanoparticles from growth and aggregation. Fig. 4 shows the UV-vis spectra of colloidal silver nanoparticles with different SDS/AgNO₃ weight ratios (0.5, 2, 5 and 20). The nanoparti-
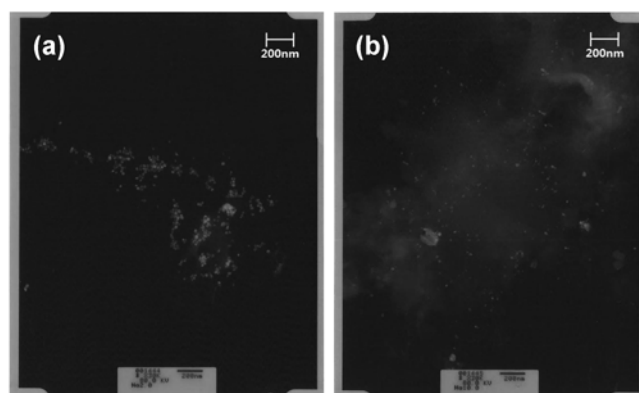

Fig. 2. UV/vis absorption spectra of the silver nanoparticles prepared with different NaBH₄/AgNO₃ molar ratios.

Fig. 3. TEM images of silver nanoparticles prepared with different NaBH₄/AgNO₃ molar ratios. (a) NaBH₄/AgNO₃=2 and (b) NaBH₄/AgNO₃=10.
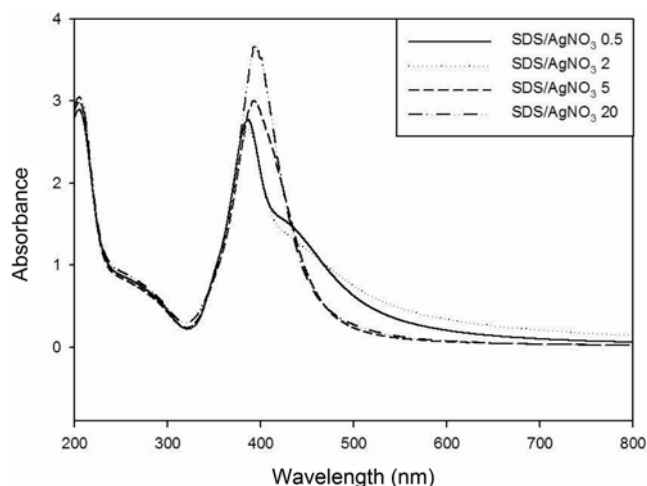
Fig. 4. UV/vis absorption spectra of the silver nanoparticles prepared with different SDS/AgNO$_3$ weight ratios.

cles were synthesized at the conditions of initial AgNO$_3$ concentration (0.001 M) and the NaBH$_4$/AgNO$_3$ molar ratio of 4. As the SDS concentration increased, the color of solutions changed from brown to yellow. At high SDS/AgNO$_3$ weight ratios (5, 20), narrow surface plasmon absorption peaks at 400 nm were observed, confirming the nanocrystalline character and well-dispersed state of the silver particles. However, when the SDS/AgNO$_3$ weight ratios were low (0.5, 2), the absorption peaks became broad, indicating that silver nanoparticles were aggregated. These results mean that when adequate amount of SDS was used, SDS absorbed on the surface of silver nanoparticles, and protected the silver nanoparticles from growth and aggregation as a result of its steric effect.

CONCLUSIONS

Silver nanoparticles were successfully prepared by reducing AgNO$_3$ with sodium borohydride in the presence of SDS as a stabilizer. The UV-vis absorption spectra showed that when excess NaBH$_4$ was used, the thick BH$_4^-$ layer prevented the boron hydroxide from absorbing to the surfaces of silver nanoparticles, resulting in well-dispersed silver nanoparticles. The TEM images showed that the degree of particle aggregation depended on different NaBH$_4$/AgNO$_3$ molar ratios. When small amount of NaBH$_4$ was used (NaBH$_4$/AgNO$_3$= 2), profound aggregation of silver nanoparticles was observed. However, with increasing the NaBH$_4$ concentration, the aggregation was reduced, and the degree of dispersion improved considerably.

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