ISSN : 0974 - 7494 Volume 5 Issue 1

Trade Science Inc.

Nano Science and Nano Technology
An Indian Journal

Full Paper

NSNTAIJ, 5(1), 2011 [28-32]

Synthesis and optical properties study of colloidal silver nanoparticles at different $AgNO_3$ concentration by chemical reduction method

Surender Duhan
Materials Science Lab, Department of Materials Science & Nanotechnology,
Deenbandhu Chhotu Ram University of Science & Technology, Murthal, Sonepat - 131 039, (INDIA)
E-mail : surender6561@yahoo.co.in

Received: 30th October, 2010 ; Accepted: 9th November, 2010

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-NIR absorption spectra, Transmission electron micrograph (TEM) and Scanning electron micrograph (SEM) images. The UV-VIS-NIR 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 and SEM images showed that the particles were dispersed better with increasing the $NaBH_4$ concentration.

KEYWORDS

Silver nanoparticles;
Chemical reduction;
SDS;
UV-Vis-NIR absorption spectra;
TEM;
SEM.

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[6-9]. The antibacterial activity of silver nanoparticles is influenced by the size of the particles, contrary to bactericide effects of ionic silver[7,9,10]. Thus, silver nanoparticles with small size and without aggregation between particles are preferable in this application.

Different methods have been used to synthesize metal oxides doped glasses/silica in powder and thin film form[11-14]. 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.

Researchers[15-17] have pointed out that the formation of metal oxides/silicates inside or at the surface of amorphous SiO_2 matrix depends mainly on the precursor used, preparation method and thermal treatment.

The problem of high processing temperature and low solubility of metals by conventional technique can be overcome by using chemical method[15]. In general, chemical method matches the demands of industries in term of preparation of materials with high density, high mechanical and thermal shock resistance, high specific surface area, compositional purity and optical grade quality[16]. Kepinski and Wolcyrz[17] prepared Nd-doped SiO_2 with different molar ratio by the impregnation method and shown that the heat treatment plays an important role in developing different phases of the binary oxides. Dimitrev et. al.[18] investigated the microstructure of thermally treated Nd-doped silica gels by complementary techniques and found that microheterogenity with amorphous phase occurred at low temperature. However, the increase of temperature leads to the increase of crystallinity and the decrease of four-fold rings.

For proper utilization of binary oxide systems, especially nanocrystalline $AgNO_3$ doped SiO_2, in scientific and technological applications require a better understanding of the phase evolution of binary oxides. Phase evolution is deeply involved in the fundamental physics of metal oxides, host matrix, heat treatment conditions and ambient atmosphere. A detailed and systematic study has been made on the influence of prolonged high temperature sintering on the microstructure of silver oxide doped silica powder and found that prolonged sintering at high temperature mainly supports the development of silver phase of $AgNO_3$ with well defined morphology. The UV-VIS-NIR spectroscopy, Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) data of the prepared samples are provided.

EXPERIMENTAL

Silver nitrate ($AgNO_3$, 99.5%) was used as the precursor to prepare silver nanoparticles. Sodium borohydride (NaBH4, 98%) and sodium dodecyl sulphate (SDS, 98%) 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 2 hours. 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)[19].

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

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[20,21]. The reverse order of reactant addition causes the immediate precipitation of silver nanoparticles.

The aggregation state of particles was observed with a UV-VIS-NIR 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. SEM studies of the samples were carried out by scanning electron microscope (JEOL-JSMT330- A 35 CF) at an accelerating voltage of 20KV.

RESULTS AND DISCUSSION

Effect of initial $AgNO_3$ concentration

Absorption spectra

Figure 1 shows the UV-VIS-NIR spectra of colloidal silver nanoparticles prepared with different initial $AgNO_3$ concentrations (0.0001 M, 0.0002 M, 0.0005 M and 0.001M). The nanoparticles were synthesized at the conditions of $NaBH_4/AgNO_3$ molar ratio of 10 and $SDS/AgNO_3$ weight ratio of 2. The color of the solutions depended on the concentration of added $AgNO_3$ solutions. With increasing the initial $AgNO_3$ concentration, the color of solution changed from yellow to brown. The absorption peak at around 400 nm in figure 1 is attributed to the surface plasmon excitation of

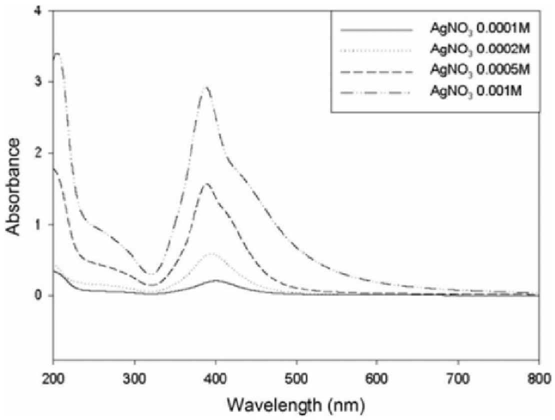

Figure 1 : UV-VIS-NIR absorption spectra of the silver nanoparticles prepared via reduction of $AgNO_3$ with different initial concentrations

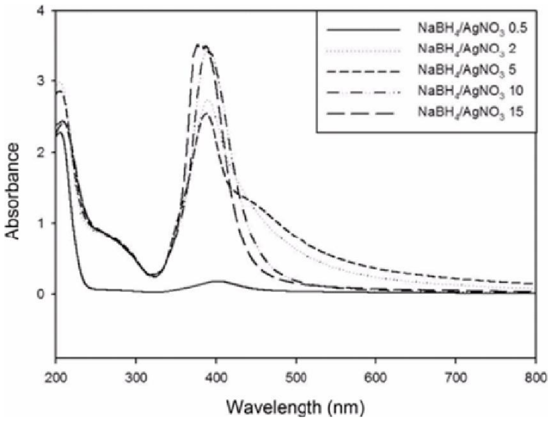

Figure 2 : UV-VIS-NIR absorption spectra of the silver nanoparticles prepared with different $NaBH_4/AgNO_3$ molar ratios

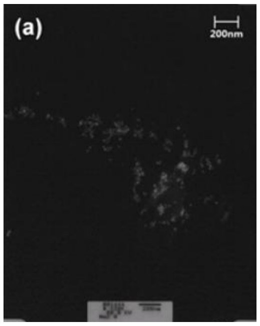

Figure 3a : TEM images of silver nanoparticles prepared with different $NaBH_4/AgNO_3$ molar ratios=2

Figure 3b : TEM images of silver nanoparticles prepared with different $NaBH_4/AgNO_3$ molar ratios=10

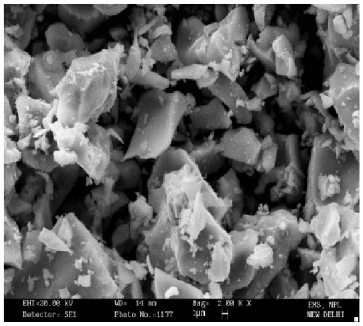

Figure 4a : SEM images of silver nanoparticles prepared with $NaBH_4/AgNO_3$ molar ratios=2

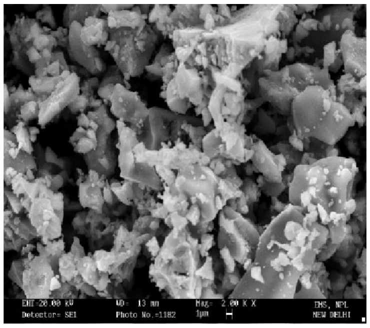

Figure 4b : SEM images of silver nanoparticles prepared with different $NaBH_4/AgNO_3$ molar ratios=10

silver nanospheres, indicating the formation of silver nanoparticles. At low $AgNO_3$ 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 $AgNO_3$ concentration, the intensity of the maximum Plasmon peak increased, indicating that higher concentrations of silver nanoparticles were formed.

Effect of $NaBH_4$ concentrations

To understand the role of $NaBH_4$ concentrations, the reduction reaction was carried out by varying molar ratios of $NaBH_4/AgNO_3$ (0.5-15) at the conditions of initial $AgNO_3$ concentration (0.001 M) and SDS/$AgNO_3$ weight ratio of 2.

UV-VIS-NIR spectra of different molar ratios of $NaBH_4/AgNO_3$ are shown in figure 2. When small molar ratio of $NaBH_4/AgNO_3$ (0.5) was used, a weak plas-

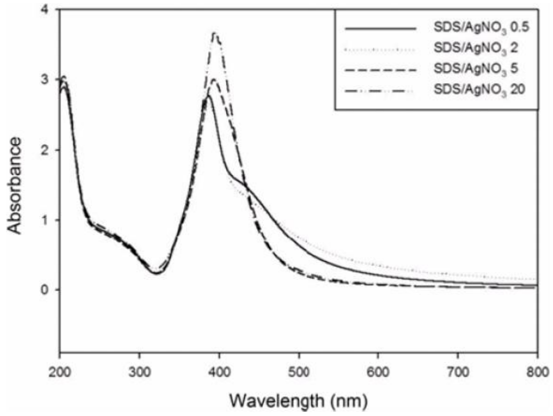

Figure 5 : UV-VIS-NIR absorption spectra of the silver nanoparticles prepared with different SDS/$AgNO_3$ weight ratios

mon 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-NIR absorption peak can give information on the degree of dispersion of silver nanoparticles[22,23]. The narrower the absorption peak, the better the degree of dispersion of nanoparticles. In the $NaBH_4/AgNO_3$ 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 $NaBH_4/AgNO_3$ 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.[21,24,25]. According to them, a small amount of $NaBH_4$ was used; the boron hydroxide produced through hydrolysis of $NaBH_4$ 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 $NaBH_4$ was used, thick BH_4 layer prevented the boron hydroxide from absorbing to the surfaces of silver nanoparticles, resulting in well-dispersed nanoparticles. These results indicate that $NaBH_4$ served not only as a reducing agent but also as a stabilizer, which protects the aggregation of silver nanoparticles. Figure 3 shows the TEM images of silver nanoparticles prepared with different $NaBH_4/AgNO_3$ molar ratios (2, 10). With increasing the $NaBH_4$ 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 $NaBH_4/AgNO_3$ molar ratios. When $NaBH_4/AgNO_3$=2, profound aggregation of silver nanoparticles was observed in figure 3a. On the other hand, in the case of $NaBH_4/AgNO_3$=10 in figure 3b, th e aggregation was reduced, and the dispersion became far better. Figure 4a and 4b shows SEM images of $NaBH_4/AgNO_3$ molar ratio (2, 10). From the figures we can see that concentration of $AgNO_3$ led to some structural refinement. Ag revealed some faceted nanostructures with decreased crystallite size in low concentration of $AgNO_3$ and increase in crystalline size in further $AgNO_3$ concentration increases which has been already confirmed by TEM analysis. As we see from micrograph with concentration $AgNO_3$ incorporated on the surface. Ag seems somewhat porous in nature. These results are well consistent with the TEM and UV-VIS-NIR spectra in figure 2.

Effect of SDS concentrations

The main purpose of introducing SDS to the solution was to prevent the silver nanoparticles from growth and aggregation. Figure 5 shows the UV-VIS-NIR spectra of colloidal silver nanoparticles with different SDS/$AgNO_3$ weight ratios (0.5, 2, 5 and 20). The nanoparticles 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-NIR 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.

REFERENCES

[1] G.Carotenuto, G.P.Pepe, L.Nicolais; Eur.Phys.J.B., **16**, 11 **(2000)**.
[2] E.Stathatos, P.Lianos; Langmuir, **16**, 2398 **(2000)**.
[3] S.V.Kyriacou, W.J.Brownlow, X.N.Xu; Biochemistry, **43**, 140 **(2004)**.
[4] X.Feng, H.Ma, S.Huang, W.Pan, X.Zhang, F.Tian, C.Cao, Y.Cheng, J.Luo; J.Phys.Chem.B, **110**, 12311 **(2006)**.
[5] S.Choi, K.S.Kim, S.H.Yeon, J.H.Cha, H.Lee, C.J.Kim, I.D.Yoo; Korean J.Chem.Eng., **24**, 856 **(2007)**.
[6] M.Kawashita, S.Tsuneyama, F.Mijaji, T.Kokubo, H.Kozuka, K.Yamamoto; Biomaterials, **21**, 393 **(2000)**.
[7] J.R.Morones, J.L.Elechiguerra, A.Camacho, K.Holt, J.B.Kouri, J.T.Ramirez, M.J.Yacaman; Nanotechnology, **16**, 2346 **(2005)**.
[8] K.S.Chou, Y.C.Lu, H.H.Lee; Mater.Chem.Phys., **94**, 429 **(2005)**.
[9] W.C.Lin, M.C.Yang; Macromol.Rapid.Commun., **26**, 1942 **(2005)**.
[10] H.S.Shin, H.J.Yang, S.B.Kim, M.S.Lee; J.Colloid. Interf.Sci., **274**, 89 **(2004)**.
[11] R.Bazzi, M.A.Flores-Gonzales, C.Louis, K.Lebbou, C.Dujardin, A.Brenier, W.Zhang, O.Tillement, E.Bernstein, P.Perriat; J.Lumin., **102**, 445 **(2003)**.
[12] W.Que, X.Hu, L.H.Gan, G.R.Deen; J.Mater.Res., **17**, 1399 **(2002)**.
[13] W.Yang, Y.Qi, Y.Ma, X.Li, X.Guo, J.Gao, M.Chen; Mater.Chem.Phys., **84**, 52 **(2004)**.
[14] M.Diaz, I.Garcia-Cano, S.Mello-Castanho, J.S.Moya, M.A.Rodriguez; J.Non-Crystal.Solids, **289**, 151 **(2001)**.
[15] J.E.Shelby, J.T.Kohli; J.Am.Ceram.Soc., **73**, 39 **(1990)**.
[16] M.Langlet, C.Coutier, W.Meffre, M.Andier, J.Fiek, R.Rinet, B.Jacquier; J.Lumin., **96**, 295 **(2002)**.
[17] L.Kepinski, M.Wolcyrz; Mater.Chem.Phys., **81**, 396 **(2003)**.
[18] Y.Dimitriev, M.Bursukova, E.Kashchieva, V.Chernev, B.Samuneva; J.Solgel Sci.Tech., **8**, 937 **(1997)**.
[19] J.P.Chen, L.L.Lim; Chemosphere, **49**, 363 **(2002)**.
[20] D.L.V.Hyning, C.F.Zukoski; Langmuir, **14**, 7034 **(1998)**.
[21] J.Liu, J.B.Lee, D.H.Kim, Y.Kim; Colloids Surf.A, **302**, 276 **(2007)**.
[22] K.D.Kim, D.N.Han, H.T.Kim; Chem.Engin.J, **104**, 55 **(2004)**.
[23] S.Kapoor; Langmuir, **14**, 1021 **(1998)**.
[24] G.A.Ozin; Adv.Mater., **4**, 612 **(1992)**.
[25] B.G.Ershov, A.Henglein; J.Phys.Chem., **97**, 3434 **(1993)**.