Controlling the Size and Morphology of Sliver Nanaoparticles: Role of Chemical Routes

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ABSTRACT

Silver Nanoparticles have been successfully synthesized by three different methods viz. solvothermal, sonochemical and microemulsion method. The role of reducing agent in the size and morphology of silver nanoparticles synthesized by sonochemical method was investigated. We have also studied the effects of surfactant in the size and morphology of silver nanoparticles synthesized from microemulsion method. These nanopowders were investigated by means of powder X-ray diffraction, transmission electron microscopy, and UV-Visible spectroscopy. Detailed surface area studies of these silver nanoparticles have been performed and observed that surface area increases with decreasing the size. The percentage yield of silver nanoparticles was found to be as high as 98.5 % synthesized by solvothermal method.

KEYWORDS: Silver Nanoparticles, Chemical methods, Surface Area, Transmission Electron Microscope, X-ray diffraction

1. INTRODUCTION

Nanostructured materials have attracted the attention of researchers because of their unusual optical, chemical, photoelectrochemical, and electronic properties [1, 2]. The applications of nanoparticles as catalysts are rapidly growing because of their size dependent electronic structure and extremely large surface area [3]. Ultrafine silver nanoparticles have many potential applications in the field of catalysis [4, 5], construction of highly sensitive and selective detectors, optical labels, nonlinear optical devices, high conductivity elements fabrication useful in printed electronics [6] and surface enhanced Raman spectroscopy [7]. Silver nanoparticles can also be used as an antimicrobial agent in various bio-medical applications [8]. Numerous chemical processes have been reported in the literature for the synthesis of silver nanoparticles such as sol-gel [9], reverse micelle [10], reduction routes [11, 12] etc. The ideal method of synthesis should yield essentially naked particles with large quantities of narrow and controlled size distribution. In order to meet such requirements we have developed a method by which we can successfully prepare silver nanoparticles by employing a modified solvothermal, sonochemical and reverse micellar method [13-15].

2. EXPERIMENTAL

The synthesis of silver nanoparticles has been carried out using modified solvothermal, sonochemical and reverse micellar method. Modified solvothermal method involves reduction of 0.1 M $AgNO_3$ solution using 0.1 M sodium borohydride followed by the addition of ethanol to form the low boiling azeotrope with water. The reaction mixture on refluxing produces silver nanoparticles which was centrifuged, washed with water and finally dried in oven. Detailed synthetic procedure is given elsewhere [13]. Silver nanoparticles were also prepared by sonochemical method using two different reducing agents viz. sodium borohydride and sodium citrate. Process I used sodium borohydride as a reducing agent. 0.1 M sodium borohydride was added to the aqueous solution of 0.1 M $AgNO_3$ dropwise under ultrasonic waves and irradiated. After the complete precipitation of the silver nanoparticles, the solution was centrifuged, washed with double distill water and finally dried in oven. Process II is similar to process I except the reducing agent. Sodium citrate was used instead of sodium borohydride. Detailed procedure is explained elsewhere [14]. Silver nanoparticles were also synthesized by reverse micellar method using three different surfactants viz. Cetyl trimethyl ammonium bromide (CTAB), Tergitol and Triton X-100. In the first reaction using CTAB as a surfactant, a single microemulsion was prepared which consists of CTAB, 1-butanol as the cosurfactant, isooctane as the hydrocarbon phase and 0.1 M aqueous solution of $AgNO_3$ as the aqueous phase. The requisite quantity of 0.1 M aqueous $NaBH_4$ solution was added dropwise and

stirred overnight. The mixture was centrifuged, washed a mixture of chloroform and methanol. The precipitate was dried in oven and finally ground to powder. The synthesis of silver nanoparticles using Tergitol as a surfactant has been carried out by mixing the two optically transparent microemulsions. These microemulsions consist of Tergitol, 1-octanol, cyclohexane and 0.1 M aqueous solution of $AgNO_3$ and $NaBH_4$ respectively. These two microemulsions were mixed and the resulting solution was heated at 65ºC in order to evaporate the solvent. Centrifuged and washed the precipitate with acetone and dried in an oven at 60ºC. Similarly silver nanoparticles have been prepared using the Triton X-100 based microemulsion system. The details of the procedure are given somewhere else [15].

To characterize and investigate the structure of the samples, the as-prepared silver nanoparticles was analyzed by Bruker D8 advance diffractometer using Ni- filtered Cu-KŬ X-rays of wavelength (ə) =1.54056Å.. The average grain size of the nanoparticles was estimated from the full width at half maximum (FWHM) of X-ray peak using the Scherrerôs formula [16]. The particle size and morphology of the sample and the corresponding selected area electron diffraction (SAED) were examined by FEI Technai G^2 20 transmission electron microscopy (TEM) with an accelerating voltage of 200 KV respectively. The N_2 adsorption isotherm, corresponding surface area and the pore parameter of the sample at liquid nitrogen temperature (78K) were recorded with B.E.T. surface area analyzer (Model Nova 2000e, Quantachrome Instruments Limited, USA) by using multiple point BET method. UV-Visible reflectance and absorbance spectra of the nanoparticles were recorded by Ocean- Optics Lambda-25 Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Structural analysis of silver nanoparticles

Figure 1 shows the powder X-ray diffraction pattern of silver nanoparticles synthesized by solvothermal method which confirmed the monophasic nature of pure silver nanoparticles with face centered cubic symmetry. The particles are spherical, highly monodisperse and uniform with an average size of ~ 5 nm (inset of figure 1). The average crystallite size evaluated by the line broadening studies and found to be 3 nm. This value agreed well with TEM observations. Similar XRD pattern were also observed for silver nanoparticles synthesized by sonochemical and reverse micellar methods [14, 15]. The camera image of silver nanoparticles is shown in figure 1(b). The percent yield of nanoparticles using solvothermal method was also calculated and found to very high (98.5 %) which is the highest reported value so far in the literature.

3.2 Particle size analysis

The size and morphology of silver nanoparticles have been obtained by transmission electron microscopy. TEM studies of silver nanoparticles synthesized by sonochemical method using $NaBH_4$ as a reducing agent showed nanorods with dimensions of 7 nm in diameter and 300 nm in length along with spherical particles having average size of 10 nm as shown in figure 2a. However, by changing the reducing agent to sodium citrate, particle size decreased to 3.5 nm (figure 2b). Particles were nearly spherical in shapes along with some icosahedral and trianguar particles. TEM images of silver nanoparticles synthesized by microemulsion method show different size and morphology by changing the surfactant which is clearly seen in figure 2(c-e). Figure 2f shows the selected area electron diffraction micrograph of silver nanoparticles. The bright spots are distributed in concentric circles which confirm the nanocrystalline nature. The ring patterns are consistent with the planes corresponding to the face centered cubic silver. All the as-prepared silver nanoparticles show similar SAED.

3.3 Optical studies

Figure 3 shows reflectance spectra of silver nanoparticles. As can be clearly seen from the spectra, besides a surface plasmon band appeared at 430 nm, silver nanopowder also gives a peak at 330 nm which may be attributed to the presence of Ag_8 silver metallic cluster [17] and a small peak at 360 nm corresponds to the surface plasmon resonance band of quasi metallic nanoparticles [18]. Apart from these peaks, some other peaks of small intensities were also appeared which have been attributed to the small charged silver clusters when synthesized by sonochemical [14] and microemulsion method. Table 1 summarizes the absorbance and reflectance spectra of silver nanoparticles synthesized by these three methods.

3.4 Surface area and Pore size studies

The surface area of the as-prepared silver nanoparticles using solvothermal, sonochemical and reverse micellar method have been determined with the help of multipoint BET equation at liquid nitrogen temperature. Table 2 summarizes the specific surface area and pore radius of the silver nanoparticles synthesized by above said methods. These results show that specific surface area of silver nanoparticles synthesized by solvothermal method comes out to be 35 m^2g^{-1} which is found to be higher than the reported value so far. It is also observed that surface area increases on decreasing the particle size. The increase in the surface area on reduction of the grain size is due to the fact that the number of surface atoms increases for a constant volume as a result surface free energy increases. The grain size of the silver nanoparticles is also calculated using the surface area studies and in all the cases, the grain sizes were found to be higher than the TEM results which may be attributed to the fact that the degassing occur at high temperature which may lead to the grain diffusion and increased in the grain sizes.

4. CONCLUSION

Highly crystalline and monophasic silver nanoparticles with cubic symmetry have been prepared successfully by three different chemical methods viz. solvothermal method, sonochemical method using two different reducing agents and microemulsion methods using three different surfactants. TEM studies show the uniform and monodisperse nanoparticles with smaller size of 5 nm with high surface area (35 m^2g^{-1}) synthesized by solvothermal method. The reducing agents also affect the size and morphology of silver nanoparticles. Particle size and morphology of silver nanoparticles were also found to be dependent on the nature of surfactants. Our study consistently showed that the surface area of silver nanoparticles increases on decreasing the grain size.

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REFERENCES

[1] L. J. Guo, X. Cheng, C. F. Chou, Nano Lett. 4 (2004) 69.
[2] Q. Xu, B. D. Gates, G. M. Whitesides, J. Am. Chem. Soc. 126 (2004) 1332.
[3] Y. C. Cao, R. Jin, J. M. Nam, C. S. Thaxton, C. A. Mirkin, J. Am. Chem. Soc. 125 (2003) 14676.
[4] X. Jiang, Y. Xie, J. Lu, L. Zhu, W. He, Y. T. Quian, Langmuir 17 (2001) 3795.
[5] Z. J. Jiang, C. Y. Liu, L. W. Sun, J. Phys. Chem. B 109 (2005) 1730.
[6] Y. Li, Y. Wu, S. B. Ong, J. Am. Chem. Soc. Commun. 127 (2005) 3266.
[7] C. L. Haynes, A. D. McFarland, R. P. Van Duyne, Anal. Chem. 77 (2005) 338A.
[8] M. Strathmann, J. Wingender, Int. J. Antimicrob. Agent 24 (2004) 36.
[9] T. Saraidarov, V. Levchenko, I. Popov, R. Reisfeld, Superlattice Microst. 46, (2009) 171.
[10] W. Zhang, X. Qiao, J. Chen, Chem. Phys. 330 (2006) 495.
[11] Y. S. Shon, E. Cutler, Langmuir 20 (2004) 6626.
[12] N. R. Jana, X. G. Peng, J. Am. Chem. Soc. 125 (2003) 1428.
[13] I. A. Wani, S. Khatoon, A. Ganguly, J. Ahmed, A. K. Ganguli, T. Ahmad, Mater. Res. Bull. 45 (2010) 1033.
[14] I. A. Wani, A. Ganguly, J. Ahmed and T. Ahmad, Mater. Lett. 65 (2011) 520.
[15] I. A. Wani, S. Khatoon, A. Ganguly, J. Ahmed and T. Ahmad (under review) Colloid Surf. A 2011.
[16] L. S. Birks, H. Friedman, J. Appl. Phys. 17 (1946) 687.
[17] P. Mulvaney, Langmuir 12 (1996) 788.
[18] P. Mulvaney, S. Underwood, Langmuir 10 (1994) 3427.

FIGURE CAPTIONS:

Figure 1. X-ray diffraction pattern of silver nanoparticles synthesized by solvothermal method. Inset shows the TEM micrograph of silver nanoparticles, (b) Camera image of silver nanoparticles.

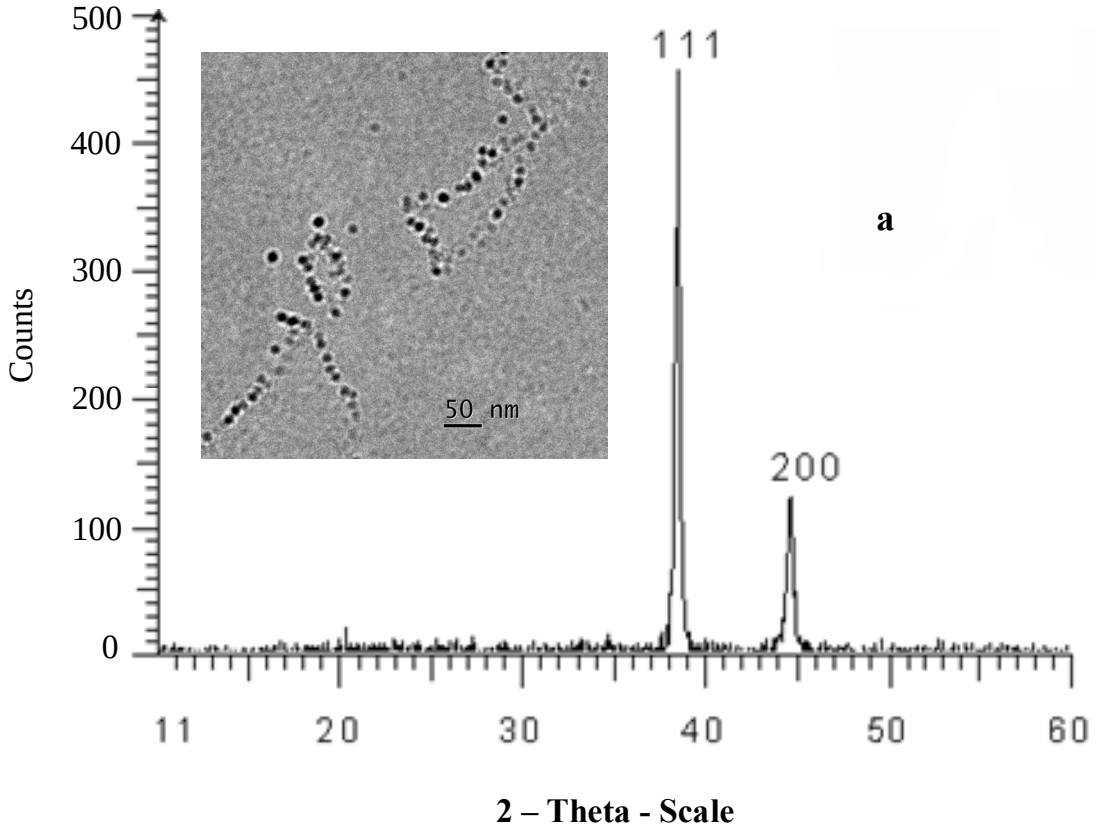
Figure 2. TEM micrographs of silver nanoparticles synthesized by (a) sonochemically using $NaBH_4$, (b) sonochemically using sodium citrate, (c) microemulsion method using CTAB, (d) Tergitol, (e) Triton X-100 and (f) SAED of silver nanoparticles synthesized by solvothermal method.

Figure 3. UV-Visible reflectance spectra of silver nanoparticles synthesized by (a) solvothermal, (b) sonochemical using $NaBH_4$, (c) sonochemical using sodium citrate, (d) microemulsion method using CTAB, (e) Tergitol, and (f) Triton X-100.

TABLE CAPTIONS:

Table 1. Absorbance and reflectance peaks of silver nanoparticles synthesized using the chemical methods.

Table 2. BET surface area, pore radius and particle size of silver nanoparticles synthesized using the chemical methods.


500
400
300
200
100
0
Counts
111
200
50 nm
a
11
20
30
40
50
60
2 – Theta - Scale


b

Figure 1

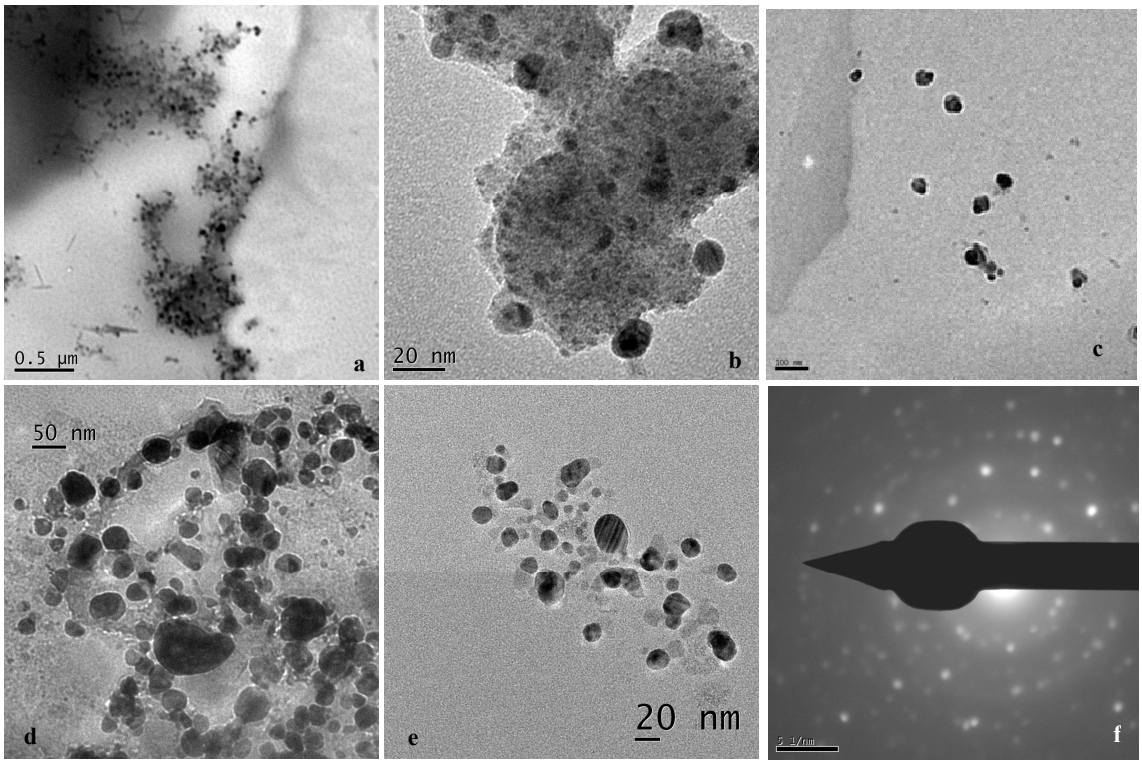


Figure 2

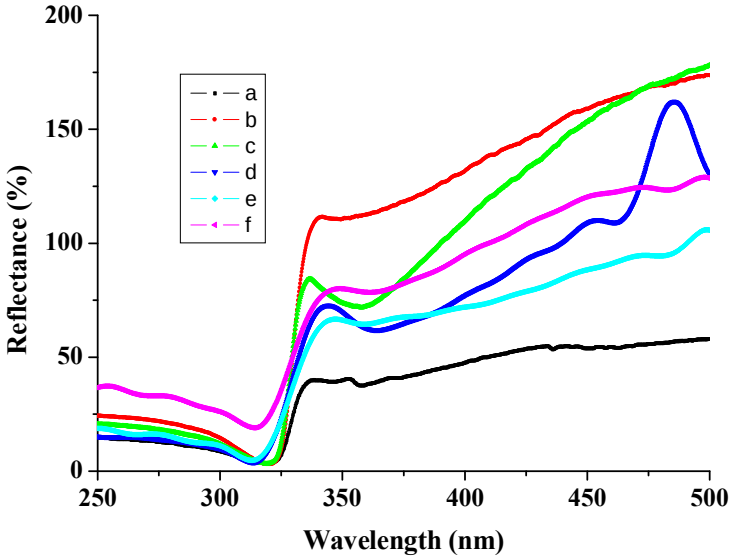


Figure 3

Method		Absorbance spectra	Reflectance spectra
Solvothermal		425 nm = SPR	430 nm = SPR 330 nm = Presence of Ag_8 metallic cluster 360 nm = SPR band of quasi metallic nanoparticles
Sonochemical	$NaBH_4$	405 nm = SPR	548 nm = SPR 360 nm = SPR of quasi spherical nanoparticles
	Sodium citrate	405 nm = SPR	535 nm = SPR 340 nm = SPR of quasi spherical nanoparticles 600 and 640 nm = quadrupolar modes exhibited by bigger particles
Microemulsion	CTAB	275 nm = Unreduced silver ions 395 nm = SPR	340 nm = Ag^{8+} and Ag^{9+} silver metal clusters 485 nm = SPR 455 nm = Higher order plasmon modes on non-spherical nanoparticles
	Tergitol	225 nm = Unreduced silver ions 395 nm = SPR	350 nm = Ag^{8+} and Ag^{9+} silver metal clusters 500 nm = SPR 470 nm = Higher order plasmon modes on non-spherical nanoparticles
	Triton X-100	250 nm = Unreduced silver ions 395 nm = SPR 310 ï 330 nm = Ag^{2+} and Ag^{9+} clusters	350 nm = Ag^{8+} and Ag^{9+} silver metal clusters 500 nm = SPR 470 nm = Higher order plasmon modes on non-spherical nanoparticles

SPR = Surface Plasmon Resonance

Table 1

Method		Particle size by TEM (nm)	BET surface area [m^2g^{-1}]	DA Pore radius [Å]
Solvothermal		5	35	9.10
Sonochemical	$NaBH_4$	10	2.6	6.5
	Sodium citrate	3.5	13.1	8.9
Microemulsion	CTAB	40	3.9	9.60
	Tergitol	30	4.2	9.40
	Triton X-100	8	15.4	8.80

Table 2