Advances in Nano Research, *Vol. 2, No. 3 (2014) 147-155*
DOI: http://dx.doi.org/10.12989/anr.2014.2.3.147

Solvothermal synthesis and characterization of silver nanoparticles

K. Venkateswara Guptha[a] and A. Samson Nesaraj[*]

Department of Chemistry, School of Science and Humanities, Karunya University, (Karunya Institute of Technology and Sciences), Coimbatore – 641 114, Tamil Nadu, India

(Received September 12, 2012, Revised September 22, 2014, Accepted September 23, 2014)

Abstract. Among the various nanoparticles reported for commercial applications, considerable interest has been generated by the use of silver nanoparticles. Owning to extremely small size, silver nanoparticles exhibit enhanced properties when compared with the bulk material. In this research work, silver nanoparticles were prepared by the reduction of silver salt with a reducing agent by a solvothermal method using different solvent mediums such as ethanol, hexane, toluene and acetone with water. The prepared silver nanoparticles were characterized systematically by X-ray diffraction (XRD), particle size analysis and scanning electron microscope (SEM). The results revealed the formation of pure silver phase and nano-sized particles. Among the different solvent mediums used, the silver nanoparticles prepared by hexane and water as solvent mixture resulted in very low particle size.

Keywords: silver nanoparticles; solvothermal synthesis; characterization

1. Introduction

In recent years, noble metal nanoparticles have been the subjects of focused researches due to their electronics, optical, mechanical, magnetic, chemical and biotechnological properties that are significantly different from those of bulk materials (Mazur 2004). Silver and its compounds have been used since the age of the ancient Egyptians, when silver vessels were used to preserve water and wine (Jorge García-Barrasa 2010). Silver nanoparticles have large surface areas and high reactivities compared with the bulk solid; thus, they exhibit remarkable physical, chemical, and biological properties, such as an increased catalytic activity because of their highly reactive facets (Nadia 2010). Recently, silver has attracted great attention due to its applications in medicinal field as anti-microbial agents (Raffi 2008). Silver, being an antimicrobial agent, has a history in wound healing dating at least 2000 years, since ancient Greece and Rome, owing to its low toxicity to human cells. For example, Berger et al. (Berger 1976) found that all 16 bacterial species they tested, including *Escherichia coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*, were inhibited by 1.25 μg/mL silver (Ag^+), while 4 μg/mL silver (Ag^+) did not exhibit any obvious detrimental effects to mouse bone marrow cells (as a susceptible normal mammalian system).

∗Corresponding author, Professor, E-mail: drsamson@karunya.edu
[a]M.Sc. Student, E-mail: venkateswaraguptha@gmail.com

http://www.techno-press.com/?journal=anr&subpage=7 ISSN: 2287-237X (Print), 2287-2388 (Online)

A number of synthetic methods for achieving controlled production of silver nano particles have been reported in the literature, but the quest is still on for more easier and commercially viable methods for production of these important nano materials. Guzmán *et al.* (2009) have prepared the silver nanoparticles by chemical reduction method. Silver nitrate was taken as the metal precursor and hydrazine hydrate as a reducing agent. The formation of the silver nanoparticles was monitored using UV-Vis absorption spectroscopy. Ana and Zhang (2008) have prepared the Polyvinyl alcohol (PVA) nanofibers containing silver nanoparticles by electrospinning PVA/silver nitrate ($AgNO_3$) aqueous solutions, followed by short heat treatment. Min *et al.* (Min 2006) have prepared the silver nanoparticles using nano-carbon as active template. Special ultrasonic condition was used to assure the active effect of the template and achieve an even and stable micro-reactor system, therefore yield uniform silver nanoparticle without obvious agglomeration. Wasif and Laga (2009) have attempted to provide antimicrobial finishing on cotton woven fabric using nano silver solution. Tiwari and Behari (2009) have studied the incorporation of silver nanoparticles (Ag-NPs) in fabrics, as anti-bacterial and fungal agent, has become a flourishing technology. Kim *et al*. (2009) have made to impart antimicrobial finishing on cotton woven fabric using nano silver solution, at various concentrations. Apart from the above literature, research efforts are being focused towards reducing the particle size of the silver particles for various applications. The present work is one such effort to synthesize silver nanoparticles by a novel solvothermal reduction process with different solvent mediums such as ethanol, hexane, toluene and acetone with water. The prepared silver nanoparticles are systematically characterized by X-ray diffraction, particle size measurements and scanning electron microscope.

2. Experimental

The reagents such as 0.1 M silver nitrate (1.6989 g $AgNO_3$ is dissolved in 100 ml of distilled water or ethanol) and 0.1M sodium borohydrate (0.37 g $NaBH_4$ is dissolved in 100 ml of distilled water or ethanol) are prepared carefully. The silver nitrate ($AgNO_3$) solution 100ml) is taken in a round-bottom flask (RB flask) (500ml capacity). The RB flask is covered with black cloth to avoid photochemical reduction of $AgNO_3$. Then, the RB flask is fitted with a magnetic stirring apparatus. To the above silver nitrate solution, sodium borohydrate solution (100ml) is added very slowly with a continuous stirring. The above mixture is thoroughly mixed for about 1 hour in the magnetic stirring apparatus. During which, the following chemical reduction reaction will take place (Ki Chang Song 2009).

$$AgNO_3 + NaBH_4 \rightarrow Ag^o + \tfrac{1}{2}\ H_2 + \tfrac{1}{2}\ B_2H_6 + NaNO_3$$

Due to the formation silver metal particles, the colour of the solution is turned as grey as reported (Christian *et al.* 2010). After this grey colouration, a suitable solvent mixture (ethanol or toluene or acetone or hexane) (100 ml) is added slowly to the above mixture. It is reported that the particles can result in a nanosized range when they are refluxed in a suitable solvent (Pablo *et al.* 2010). Hence, the RB flask is fitted with a condenser and refluxing is carried out for about 40 hours continuously at the temperature of 80^{o}C. After 40 hours of refluxing, the resultant silver nano particles are filtered suitably and air dried for further characterization. The flow chart to prepare silver nanoparticles by solvothermal process is indicated in Fig. 1. The powder XRD study was carried out using a Shimadzu XRD6000 X-ray diffractometer using Cu$K\alpha$ radiation. The unit cell parameters were calculated from the XRD data. The crystallite sizes of the silver nanoparticles

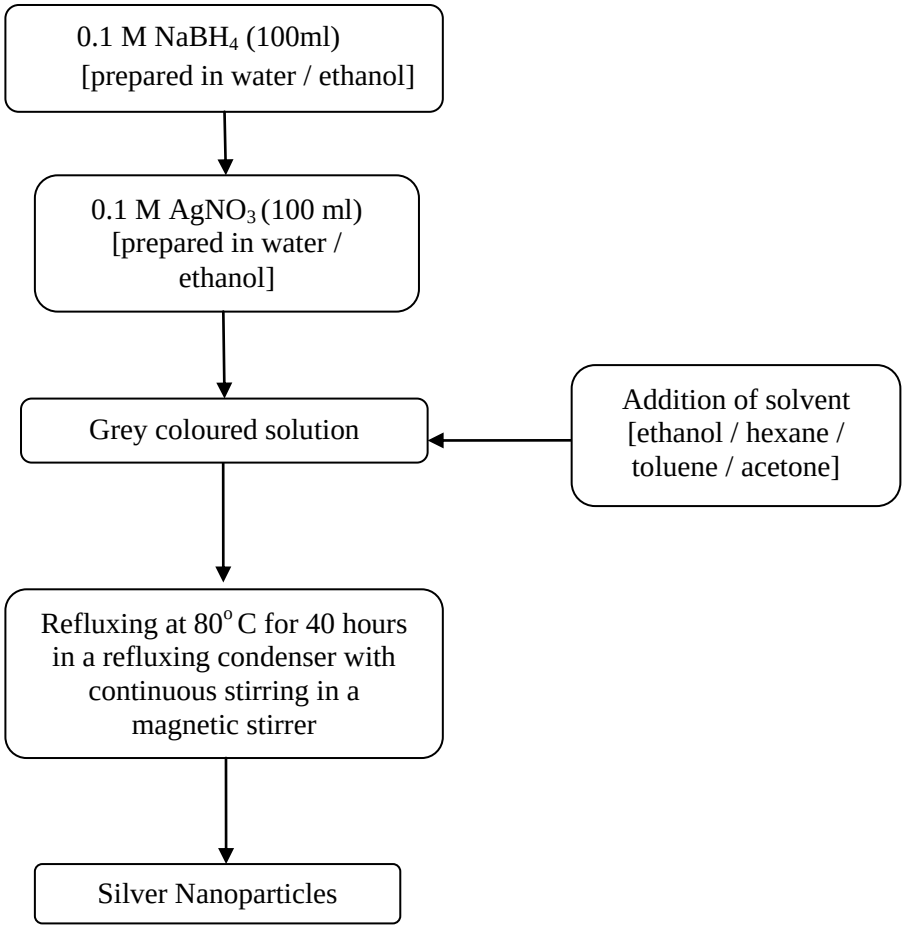

Fig. 1 Flow chart to prepare silver nanoparticles by solvothermal process

were calculated by Scherrer's formula. The particle size of the powder was measured using a Malvern Particle Size Analyzer using triple distilled water as medium. The morphology of the particles was studied by means of JEOL Model JSM-6360 scanning electron microscope (SEM).

3. Results and discussion

3.1 Structure from powder X-ray Diffraction (XRD)

Figs. 2 (a)-(e) shows the XRD patterns obtained on silver nanoparticles prepared by solvothermal process with different solvent mediums, such as, ethanol+water; hexane + water, toluene + water; acetone +water and pure ethanol and which are indexed to the face centred cubic (FCC) geometry. The XRD patterns of silver are compared with the standard JCPDS data (card No. 89-3722). The lattice parameter is calculated from 2θ values in the X-ray diffraction pattern. The crystallite sizes of the powder are calculated from the X-ray diffraction peak intensity analysis

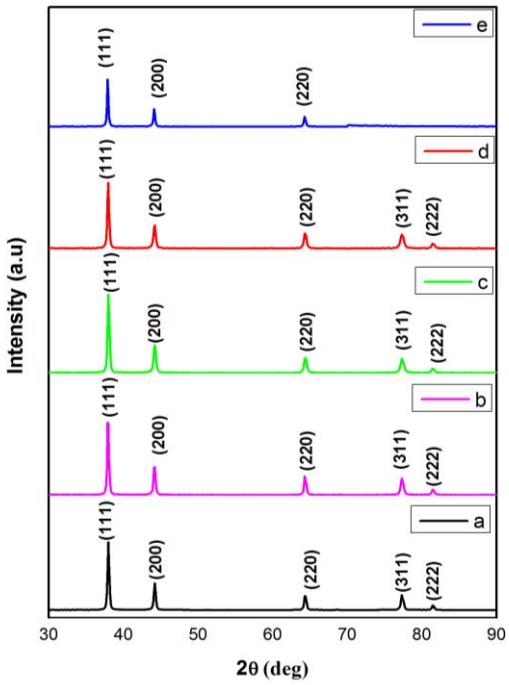

Fig. 2 X-ray diffraction pattern obtained on silver nanoparticles synthesized by solvothermal process in (a) ethanol + water mixture; (b) hexane + water mixture; (c) toluene + water mixture, (d) acetone + water mixture; (e) pure ethanol

using the Scherror formula mentioned below

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

In Eq. (1), D is crystallite size in nm, λ is the radiation wavelength (for CuKα radiation, λ=1.5418 Å), θ is the diffraction peak angle and β is the broadening of the line ("half width") measured at half its maximum intensity (in radians). Theoretical or X-ray density has been calculated (in gcm^{-3}) using the lattice parameters with the formula

$$D_{th} = z\frac{M}{N \times V} \tag{2}$$

In Eq. (2), M (in atomic-weight units) is the mass of atomic ensemble constituting one unit of the chemical formula, z is the number of such chemical units in one unit cell of the crystal, N is the Avagadro's number and V (in $Å^3$) is the volume of the crystalline unit cell as determined by X-ray diffraction. Varshney *et al*. (2009) have synthesized silver nanoparticles through a biotechnological route using fungus *Hormoconis resinae* and shown that the sample exhibited FCC geometry. Jiang *et al.* (2005) have prepared dendritic silver nanoparticles by a soft solution technique from the aqueous solution of silver nitrate and poly (vinyl pyrrolidone) (PVP) in the presence of ethanol used as a reducing agent and found that the sturucture as FCC. Ganesh Babu and Gunasekaran (2009) have produced crystalline silver nanoparticles from *Bacillus cereus*

Table 1 Crystallographic properties obtained on silver nanoparticles prepared by solvothermal process

Powder / Solvent mixture	Crystal structure	Unit Cell parameter- 'a' (Å)	Unit cell volume (Å ^{3})	Theoretical density (g/cc)	Crystallite size (nm)
Ag/ Reported in JCPDS No. 89-3772	FCC	4.085	68.167	10.510	12.236
Ag/ Ethanol + Water	FCC	4.088	68.321	10.499	12.237
Ag/ Hexane + Water	FCC	4.276	78.189	9.162	13.342
Ag/ Toluene + Water	FCC	4.239	76.186	9.403	18.115
Ag/ Acetone + Water	FCC	4.093	68.611	10.441	33.356
Ag/ Pure Ethanol	FCC	4.1034	69.092	10.369	12.225

isolate and they reported the structure of silver nanoparticle as FCC. By comparing the XRD patterns with the standard JCPDS pattern (card No. 89-3722), it was found that the particles were confirmed as elemental Ag (0). No other peaks corresponding to any other impurity are observed in the XRD patterns of the silver particles synthesized by solvothermal process in different mediums. The crystallographic properties obtained on silver nanoparticles prepared by solvothermal process with different mediums are presented in Table 1. From the crystallographic data, it was understood that the observed unit cell parameter (=*a*) for all the samples are in agreement with the reported JCPDS data except with small deviations. However, it was found that the unit cell parameters of silver nanoparticles prepared with the solvent mixtures hexane with water and toluene with water are found to be larger. Since hexane and toluene are non-polar solvents, they are immiscible with water, because water is a polar solvent. Hence, immiscible solvent mixture can influence the structural characteristics of the sample. From the XRD data, it was found the samples prepared with miscible solvent mixtures resulted in unit cell parameters which are in good agreement with the reported JCPDS data. There is no trend observed from the observed density data. The XRD peak broadening shows that the crystalline sizes of the resulting silver nanoparticles remained small except the sample prepared with acetone + water system. The values ranged between 10-33 nm. The density and crystallite size values obtained are in accordance with the data reported earlier (Zhou *et al.* 2009).

3.2 Particle characteristics

The prepared silver particles were subjected to particle size measurements using Malvern particle size analyzer with triple distilled water as medium. For all the measurements, 0.20 g of sample is sonicated in 200 ml triple distilled water for about 5 minutes and after that the sample is subjected for particle size analysis. The particle size distribution curves (based on volume) of silver are shown in Figs. 3 (a)-(e). The particle size data is given in Table 2. From the particle characteristics of the silver nanoparticles, it was found that the particles are present in the nm range. As well as, it was clearly understood the particles are present in lower size range. Further, it was found that the particles prepared with immiscible solvent mixtures (hexane with water and toluene wit water) resulted in big particle size when compared with the particles with miscible solvent mixtures. From this, we came to know that the particles can agglomerate easily to become bigger size particles if they were present in immiscible solvent medium (Yadav and Yadav 2009).

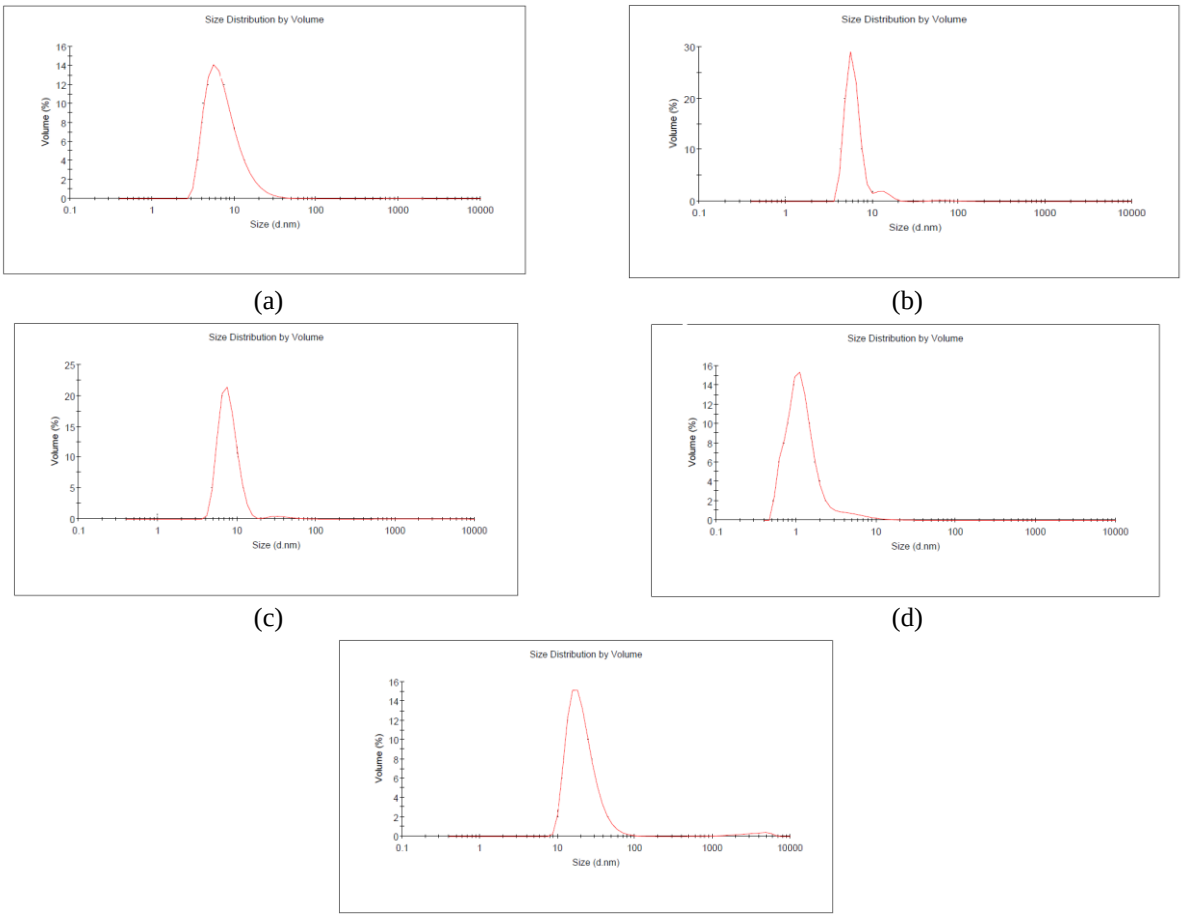

Fig. 3 Particle distribution curves obtained on silver nanoparticles synthesized by solvothermal process in (a) ethanol + water mixture; (b) hexane + water mixture; (c) toluene + water mixture, (d) acetone + water mixture; (e) pure ethanol

3.3 Microstructural studies

The surface microstructures of silver powder were studied with SEM. The arrangement of grains, size of grains, etc. were differed for the samples based on the preparative conditions. Figs. 4(a)-(e) shows the SEM photographs obtained on the silver nanoparticles in different solvent mediums. The grain size of silver prepared with ethanol + water mixture is in the range of 100 nm (Fig. 4(a)). From the Fig. 4(b), it was understood that the grain size is in the range of 54-80 nm. Also, in Fig. 4(b) (prepared with hexane + water mixture), the grains are not present separately rather they are present together. In Fig. 4(c) (prepared with toluene + water mixture), it was found that the particles are present in the bigger size range (around 1 μm). In the sample prepared with acetone + water medium (Fig. 4(d)), it was found that the grains are present in larger size range (more than 1 μm). For the sample prepared with pure ethanol as solvent medium, it was found that the grain size is in the range of 100-150 nm. As indicated in the XRD analysis and particle

Table 2 Particle characteristics data (based on volume) obtained on silver nanoparticles prepared by solvothermal process

Trial	Peak 1		Peak 2		Peak 3		Average particle size (nm)
	% volume	Diameter (nm)	% volume	Diameter (nm)	% intensity	Diameter (nm)	
Ethanol + Water	99.9 %	7.7948	0.1 %	1210	--	--	17.86
Hexane + Water	1.1 %	71.15	91.5 %	6.009	7.4 %	13.25	59.36
Toluene + Water	2.5 %	36.11	0.40 %	2.393	97.1 %	7.869	33.64
Acetone + Water	100 %	1.422	--	--	--	--	8.219
Pure Ethanol	97.0 %	21.69	3.0 %	3.434	--	--	34.13

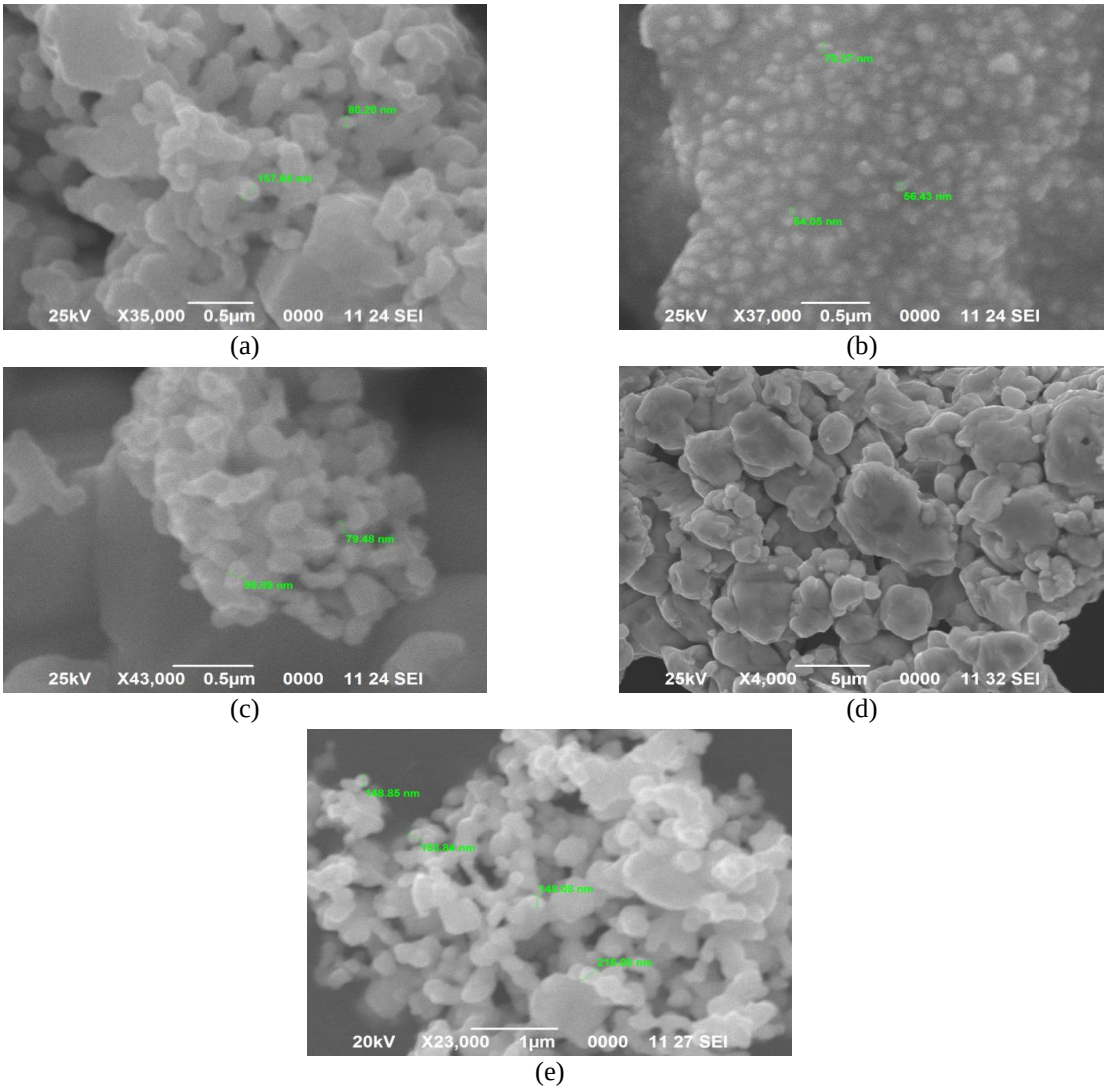

Fig. 4 SEM photograph obtained on silver nanoparticles synthesized by solvothermal process in (a) ethanol + water mixture; (b) hexane + water mixture; (c) toluene + water mixture, (d) acetone + water mixture; (e) pure ethanol

characteristics, the samples prepared in immiscible solvent mixtures resulted in bigger grain size.

4. Conclusions

Synthesis of silver nanoparticles by solvothermal process using different solvents is dealt with. The powder XRD data obtained on silver powder is in good agreement with the standard reported XRD data. The particle characteristics data revealed the presence of nano sized particles in the silver powder. The Scanning Electron Microscope (SEM) studies also confirmed the presence of nano sized particles. The silver particles prepared with hexane + water medium have shown excellent particulate properties in total with all the measurements.

Acknowledgements

ASN thanks the Administration of Karunya University for promoting nanotechnology research activity at Karunya University.

References

An, J., Zhang, M., Wang, S. and Tang, J. (2008), "Physical, chemical and microbiological changes in stored green asparagus spears as affected by coating of silver nanoparticles-PVP", *LWT-Food Sci. Tech.*, **41**, 1100-1107.

Berger, T.J., Spadaro, J.A., Chapin, S.E. and Becker, R.O. (1976), "Electrically generated silver ions: quantitative effects on bacterial and mammalian cells", *Antimicrob. Agents. Chemother*., **9**, 357-358.

Christian, K., Radian, P., Erich, M., Dagmar, G. and Claus, F. (2010), "Microemulsion-based synthesis of nanoscaled silver hollow spheres and direct comparison with massive particles of similar size", *Nanoscale*, **2**, 2223-2229.

Dhermendra, K.T. and Behari, J. (2009), "Biocidal nature of combined treatment of Ag-nanoparticle and ultrasonic irradiation in *Escherichia coli dh5*", *Adv. Biolog. Res.*, **3-4**, 89-95.

Ganesh Babu, M. and Gunasekaran, P. (2009), "Production and structural characterization of crystalline silver nanoparticles from *Bacillus cereus* isolate", *Coll. Surf. B: Biointerf.*, **74**, 191-195.

Heng, M., Wand, Z.S. and Zhu, Y.W. (2006), "Preparation of silver nanoparticle via active template under ultrasonic", *Tran. Non Ferr. Met. Soc. China*, **16**, 1348-1352.

Jiang, G.H., Wang, L., Chen, T., Yu, H.J. and Wang, J.J. (2005), "Preparation and characterization of dendritic silver nanoparticles", *J. Mater. Sci.*, **40**, 1681-1683.

García-Barrasa, J., López-de-Luzuriaga, J.M. and Monge, M. (2010), "Silver nanoparticles: synthesis through chemical methods in solution and biomedical applications", *Centr. Euro. J. Chem.*, **9**, 7-19.

Guzmán, M.G., Dille, J. and Godet, S. (2009), "Synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity", *Int. J. Chem. Biomol. Eng*., **2**, 104-111.

Guardia, P., Prez, N., Labarta, A. and Batlle, X. (2010), "Controlled synthesis of iron oxide nanoparticles over a wide size range", *Langmuir*, **26**, 5843-5847.

Kim, T.H., Kim, K., Park, G.H., Choi, J.H., Lee, S., Kang, H.J., Lee, J.Y. and Kim, J. (2009), "Preparation and characterization of water-dispersible silver nanoparticles stabilized by PEO-conjugated pro-drugs", *Macromol. Res.*, **17**, 770-775.

Mazur, M. (2004), "Electrochemically prepared silver nanoflakes and nanowires", *Electrochem. Commun.*, **6**, 400-403.

Nadia, G.K., Howida, T.Z., Mansoura, I.M. and Hemat, M.M. (2010), "Silver nanoparticles effect on

antimicrobial and antifungal activity of new heterocycles", *Bull. Korean Chem. Soc*., **31**, 3530-3538.
Raffi, M., Hussain, F., Bhatti, T.M., Akhter, J.I., Hameed, A. and Hasan, M.M. (2008), "Antibacterial Characterization of Silver Nanoparticles against *E: Coli* ATCC-15224", *J. Mater. Sci. Technol.*, **24**, 192-196.
Song, K.C., Lee, S.M., Park, T.S. and Lee, B.S. (2009), "Preparation of colloidal silver nanoparticles by chemical reduction method", *Korean J. Chem. Eng.*, **26**, 153-155.
Varshney, R., Mishra, A.N., Bhadauria, S. and Gaur. M.S. (2009), "A novel microbial route to synthesize silver nanoparticles using fungus *Hormoconis resinae*", *Digest J. Nanomater. Biostruct.*, **4**, 349-355.
Wasif, A.I. and Laga, S.K. (2009), "Use of nano silver as an antimicrobial agent for cotton", *Autex Res. J.*, **9**(1), 1348-1352.
Yadav, V.B. and Yadav, A.V. (2009), "Polymeric recrystallized agglomerates of Cefuroxime Axetil prepared by emulsion solvent diffusion technique", *Trop. J. Pharmaceut. Res*., **8**(4), 361-369.
Zhou, M., Wei, Z., Qiao, H., Zhu, L., Yang, H. and Xia, T. (2009), "Particle size and pore structure characterization of silver nanoparticles prepared by confined arc plasma", *J. Nanomater.*, 1-5.

YH