Synthesis, Spectral Characterization and Anti-Microbal Activity of Silver Nanoparticles in 1-Alkyl–3-Methylimidazolium Methanesulfonate Ionic Liquids

Ayi A. Ayi*, Aniefiok J. Umoh, Chinyere A. Anyama, Samuel S. Etuk and Joseph O. Ogar
Department of Pure and Applied Chemistry,
University of Calabar, P.M.B. 1115-Calabar, Nigeria

Abstract:- Nanoparticles of silver have been synthesized via the reaction of silver nitrate salt in 1-akyl-3-methylimidazolium methane sulfonate ionic liquids. The reaction was performed under reducing conditions in the presence of NaBH4 and at elevated temperatures to obtain homogeneous reaction mixtures. The FTIR of samples in both EMIMMS and BMIMMS shows pronounced absorption at 3426cm-1, assignable to the symmetric stretching vibration of v(N-H) group of the imidazolium cation. The bands between ca. 3100 cm-1 along with the bands between 1,600 and 1,500 cm-1 can be assigned to C–H stretching and in-plane vibrations of the imidazolium ring. The bands between 1,300 and 1,050 cm-1 can be assigned to aliphatic in-plane vibrations, and the bands between 900 and 750 cm-1 are due to the respective out-of- plane vibrations of the organic cations, respectively. The UV-Vis absorption spectra of samples shows surface plasmon resonance (SPR) band (λmax) around 420 nm for EMIMMS, which becomes broadened and slightly shifted to the longer wavelength region of 620 nm for BMIMMS ionic liquids indicating the presence and formation of silver nanoparticles. The SEM images confirm that the precipitates are indeed nanoparticles. The SNPs grown in both EMIMMS and BMIMMS consists of clusters of nanoplates and nanorods. The results of the antimicrobial activity carried out on some selected microbes showed that the silver nanoparticles synthesized in 1-butyl-3-methyimidazolium methane sulfonate and the ionic liquid itself showed a greater zone of inhibitory clearance compared to the silver nanoparticles synthesized in 1-Ethyl-3-methylimidazoliumethane sulfonate.

Key words: Nanoparticles, Ionic liquids, silver, chemical reduction, ionothermal, antimicrobial activity.

I. INTRODUCTION

Nanoparticles which could be particulate dispersions or solid particles are basically assemblies of hundreds to thousands of atoms with a size in the range of 1-100nm. These nanomaterials are quite interesting for a large variety of applications, including catalysis, sensing, and electrochemistry [1-4]. Silver nanoparticles in particular are attractive because of their unique optical and disinfectant properties. They are used for many different applications and in a wide range of different products [5,6]. In the medical field, they are non-toxic to the human body at low concentrations and have broad spectrum of antibacterial actions [7,8]. Consequently, they are applied in wound dressing, as well as for coating of working surfaces or surgical instruments and prostheses [9, 10]. Silver nanoparticles can also be used in food container systems or as coating material for certain household devices such as washing machines [11]. They are incorporated into textiles [12-13], and even added to cosmetics [14]. The performance of nanomaterials in many of these applications requires the control over the size, the morphology and the surface structure, which is based on the appropriate control of the parameters that influence nucleation and growth [15-17]. There is thus a need to control these parameters for efficient operation of a device or device component. While there are many protocols available for the synthesis of metallic nanoparticles, ionic liquids have been investigated as candidates for the synthesis of many metal nanoparticles [15], including titanium and/ or titanium oxide and gold nanoparticles [18-19], because ILs have in the recent past been established as useful media for the synthesis of a wide variety of inorganic materials [20-25]. Among others, metal nanoparticle formation in ILs and their application have attracted interest because many ILs efficiently stabilize nanoparticles under a variety of experimental conditions. The particular interest in ILs is that they can also stabilize inorganics (not only nanoparticles) that cannot be stabilized otherwise. The current study reports on an ionic liquid assisted synthesis of silver nanoparticles via chemical reduction of $AgNO_3$ by $NaBH_4$ under quasi-ionothermal conditions.

II. EXPERIMENTAL MATERIALS

ILs based on 1-ethyl-3-methylimidazolium (Emim) or 1-butyl-3-methylimidazolium (Bmim) cations and methanesulfonate(MS), AgNO3, NaBH4 ,ethylene glycol were obtained commercially (BHD chemical Ltd. England) and used as received.

Nanoparticle synthesis

In a typical synthesis, , 0.043 g (0.25mmol) of silver trioxonitrate(V) salt was added to 1 g of IL. The mixture was sonicated for 10 min. Then 0.0038 g (1 mmol) of $NaBH_4$ was added at ambient conditions. The resulting dark mixture was stirred and heated to about 120 ^oC for 8hr. Before isolating the precipitate by centrifugation, a small fraction of the dark colloidal dispersion was removed for UV/Vis, and IR measurements. The centrifuged product was washed with ethanol and dried under vacuum for 12 h.

Spectroscopy

FTIR spectra of the solid samples prepared using KBr pellets were recorded between 4000-400 cm-1 on Perkin Elmer FTIR spectrophotometer at 2 cm-1 resolution. The UV/Vis spectrophotometric measurements were performed on Thermo scientific evolution 201 spectrometer using 10mm quartz cuvettes containing the nanoparticles. The samples were dissolved in ethyleneglycol then transferred into a cuvette before being placed in the spectrophotometer for the detection of the absorbance. The UV/Vis absorption spectral data of the fraction of the nanoparticles in ionic liquid (as well as the solid gathered by centrifugation) dispersed in ethanol were collected at room temperature.

Scanning Electron Microscopy (SEM)

The images of the compound were obtained with the aid of Scanning Electron Microscope- mini MEL-300M SCO-TECH operated at 15kV.

Antimicrobial Activity Test

Muller Harting algar dilution technique sensitizing test was carried out on the ionic liquids and the filtrate of the synthesized silver nanoparticles, this was done on the spectrum of microbial organisms. Using the porous cud, the agar well was created on the solidified broth which was prepared by dilution of an overnight broth culture in a petri dish, with the help of 2.0ml syringe, the filtrate was introduced into the well and was left to stand overnight after which a ruler was used to measure the minimum inhibitory zone of clearance (MIC) expressed in (cm), the values after one day of exposure were recorded.

Results and Discussion

Silver nanoparticles have been synthesized by chemical reduction of silver trioxonitrate (V) in ionic liquids based on 1-ethyl-3-methylimidazolium (EMIM) or 1-buthyl-3-methyl imidazolium (BMIM) cations and methane sulfonate (MS) anion. The reactions were performed under quasi-ionothermal conditions in the presence of $NaBH_4$ at 120^oC to obtain homogeneous reaction mixtures

$$AgN0_3 + IL \xrightarrow{NaBH_4} Ag(0) - Nanoparticles$$
$$IL = \quad [EMIM][MS] \; or \; [BMIM][MS]$$

The dispersion of the metal salt in ionic liquid gives a brownish colouration, which changes to black on addition of sodium borohydride. A small fraction of the brownish and black colloidal dispersion representing Ag+-

IL and Ag0-IL interactions, respectively, was taken for IR and UV-Vis measurements before heating under reflux at 120oC. The UV-Vis spectrum of Ag+-EMIMMS mixture at room temperature (30oC) shows that there is an interaction between the ionic liquid and the silver ion resulting in the formation of brownish solution. The gradation in colour from colorless to brown is an indication of self-reduction of the Ag ion by the EMIMMS ionic liquid. On addition of the reducing agent, reduction of the Ag ion to Ag0 takes place as evidenced by the change in colour from brown to black, as well as by intense absorption in the range of 200-240nm centered at 210nm in the UV region ascribed to ligand-to-metal charge transfer (LMCT). This represents a discrete nucleation event with molecules of the ionic liquid being adsorbed on the surface of the Ag0 nanoparticles. The nucleation is followed by slower controlled growth, which on heating, the particles acquire enough surface energy that promotes dissolution and second growth phase (Ostwald ripening) with the formation of uniform mono- dispersed larger particles [26-30]

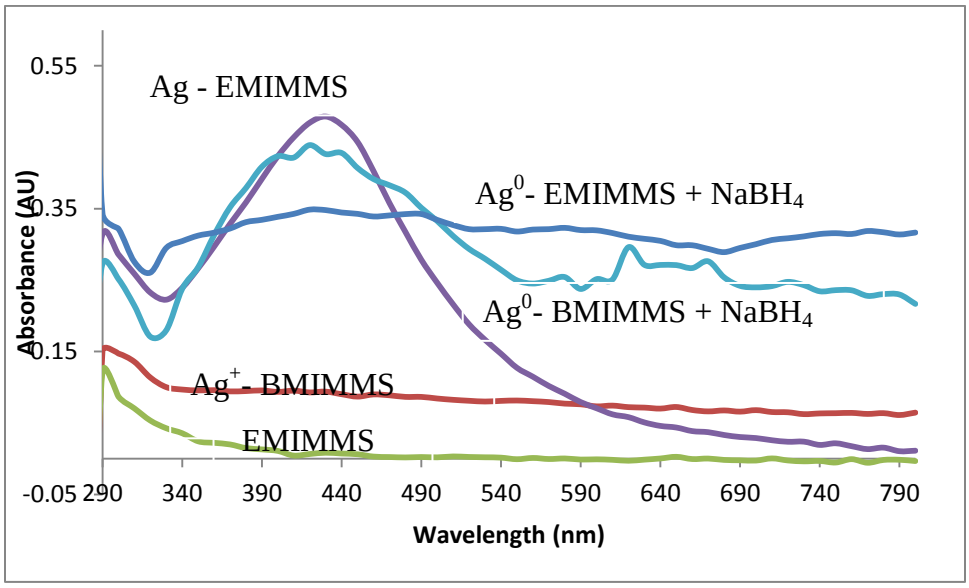


Fig1. UV-Vis absorption spectra of silver nanoparticles in EMIMMS and BMIMMS ILs

Figure 1 gives the UV-Vis spectra of the silver nanoparticles grown in imidazolium-based ionic liquids after 8h of heating at 120oC. The UV-Vis absorption spectra of ionic liquid-stabilized silver nanoparticles shows that after the borohydride reduction of the Ag+ to Ag nanoparticles, the wavelength at absorption maximum (λmax) for the nanoparticles shift towards longer wavelength and exhibits band broadening in the range 330-580nm . The wavelength at absorption maxima (λmax = 420nm) can be attributed to the presence of particles in the size range 2-50nm. The shift towards longer wavelength of 580nm and 630nm, respectively for EMIMMS and BMIMMS clearly indicates the presence of larger particles. The position and shape of plasmon absorption of silver nano-clusters are strongly dependent on the particle size, dielectric medium, and surface-adsorbed species. The surface plasmon absorption of silver nanoparticles have short wavelength band in the visible region around 420 nm due to the transverse electronic oscillation [31].

The infrared spectra of samples grown in EMIMMS and BMIMMS shows common absorption bands in the samples isolated even after centrifugation and washing. A pronounced absorption at 3426cm-1, is assignable to the symmetric stretching vibration of v(N-H) group of the imidazolium cation. The bands between ca. 3100 cm-1 along with the bands between 1,600 and 1,500 cm-1 can be assigned to C–H stretching and in-plane vibrations of the imidazolium ring. The bands between 1,300 and 1,050 cm-1 can be assigned to aliphatic in-plane vibrations, and the bands between 900 and 750 cm-1 are due to the respective out-of- plane vibrations of the organic cations, respectively. The band at 1310-1373cm-1 region is attributed to the v(C-N) stretching vibration of the tertiary amine. Also the vibration at 726 cm-1 indicates the presence of v(C-S) stretching vibration of the

methanesulfonates, while the absorption band at 1373 – 1456.48cm-1 region is a clear indication of the presence of sulfonates vibration. The various assignments are in agreement with similar compounds reported in literature [32-34].

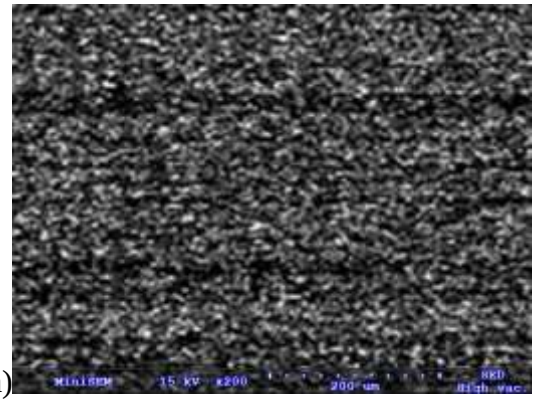
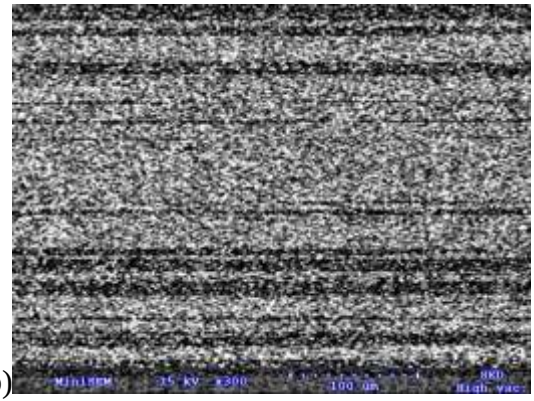
a)  b) 

Fig.2 SEM images of silver nanoparticles grown in ionic liquids a) EMIMMS b) BMIMMS

The SEM images of MNPs grown in both EMIMMS and BMIMMS ionic liquids are presented in Figure 2. The images confirm that the precipitates are indeed nanoparticles. The SNPs grown in both EMIMMS and BMIMMS consists of clusters of nanoplates and nanorods. There is a slight increase in both the nanoparticles diameter and size distribution as we move from C2 to C4 of the alkyl-side chains of the imidazolium cation.

Nanoparticles must be stabilized in order to prevent their agglomeration or aggregation which eventually leads to the formation of small bulk metal particles. Metal nanoparticles (M-NPs, "core") are considered stabilized in ILs by the formation of "protective" anionic and cationic layers ("shells") around them in a "core-shell system". The first inner shell is believed to be anionic, [35] because then the IL anion would have the strongest influence on the size and electrostatic stabilization and the anion molecular volume controls the range of the nanoparticle size. In addition, the supramolecular imidazolium-anion clusters of ILs should be taken into account [36].

Table 1 gives the anti-bacterial activity of the silver nanoparticles prepared in EMIMMS and BMIMMS ionic liquids. The results shows that the silver nanoparticles synthesized in 1-butyl-3-methyimidazolium methane-sulfonate and the ionic liquid itself showed a greater zone of inhibitory clearance compared to the silver nanoparticles synthesized in 1-ethyl-3-methylimidazoliumethane sulfonate. This result is in line with the literature report that the microbial activity of the nanoparticles depends on the length of the alkyl side chains, and the positions they are being attached to the imidazolium ring [30, 37].

TABLE 1 Anti-microbial Activity Test

Samples	MIC on tested microbes					
	STA	PRT	ES	CA	PA	ST
BMIM[MS]	1.4	2.2	3.4	2.0	2.1	R
EMIM[MS]	1.4	2.5	2.8	1.1	1.6	R
AgEMIM[MS]	1.0	1.3	R	R	1.2	R

AgBMIM[MS]	2.0	1.1	1.8	R	1.6	R

STA: StaphylocusAureus, PRT: Proteus, ES: Escherichia Coli,
CA: Candida alblicans, PA: Pseudomonas aerogerosa, ST: Salmonella typhi,

III. CONCLUSION

Silver nanoparticles have been successfully synthesized in 1-ethyl-3-methylimidazoliu methane sulfonate and 1-butyl-3-methyimidazolium methane sulfonate ionic liquids by chemical reduction of $AgNO_3$ in the presence of $NaBH_4$. The dispersion of the metal salt in ionic liquid gives a brownish colouration, which changes to black on addition of sodium borohydride. IR and UV-Vis measurements reveal that the ionic liquids are adsorbed on the surface of the silver nanoparticles thereby providing electrostatic stabilization of the particles. There is clear evidence from the UV-Vis measurement that the ionic liquid 1-ethyl-3-methylimidazolium methane sulfonate (EMIMMS) can as well act as a reducing agent. The SEM micrographs shows the presence of uniformed monodispersed nanorods in both EMIMMS and BMIMMS ionic liquids. The anti-microbial test reveals that the silver nanoparticles prepared in BMIMMS has greater zone of inhibitory clearance. Efforts are under way to prepare the metal nanoparticles in a wide spectrum of imidazolium-based ionic liquids.

ACKNOWLEDGEMENT

This work was supported by The World Academy of Sciences for the advancement of science in developing countries (TWAS) under Research Grant No 12-169 RG/CHE/AF/AC-G -UNESCO FR: 3240271320 for which grateful acknowledgment is made. A.A.A is also grateful to the Royal Society of Chemistry for personal Research Grant.

REFERENCES

[1] Caruso, F., *Colloids and Colloid Assemblies*, Weinheim: Wiley-VCH. 2004.

[2] Bergna, H. E. and Roberts, W. O., *Colloidal Silica - Fundamentals and Applications*. Surfactant Science Series, Vol. 131. Boca Raton - London - New York: Taylor & Francis, 2006.

[3] Daniel, M.C. and Astruc, D.(2004) *Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. Chem. Rev.*. **104**(1): p. 293.

[4] Zhang G, Niu A, Peng S, Jiang M, Tu Y, Li M, Wu C (2001) Formation of novel polymeric nanoparticles. *Acc Chem Res* **34,**249-256

[5] Edward-Jones V (2009), The benefits of silver in hygiene, personal care and healthcare. *Lett Appl Microbiol* **49**, 147–152

[6] Chen X, Schluesener HJ (2008) Nanosilver: a nanoproduct in medical application. Toxicol Lett 176, 1–12

[7] Baker C, Pradhan A, Pakstis L, Pochan DJ, Shah SI (2005),Synthesis and antibacterial properties of silver nanoparticles. J Nanosci Nanotechnol 2005, 5:244-249.

[8] Rai M, Yadav A, Gade A: (2009), Silver nanoparticles as a new generation of antimicrobials. *Biotechnol Adv* 2009, 27:76-83.

[9] Eby DM, Luckarift HR, Johnson GR (2009), Hybrid antimicrobial enzyme and silver nanoparticle coatings for medical instruments. *ACS Appl Mater Interf* **1**, 1553–1560

[10] Jain J, Arora S, Rajwade JM, Omray P, Khandelwal S, Paknikar KM (2009) Silver nanoparticles in therapeutics: development of an antimicrobial gel formulation for topical use. *Mol Pharmacol* 6,1388–1401

[11] Haase, A., Mantion, A., Graf, P., Plendl, J., Thuenemann, A.F., Meier, W., Taubert, A., Luch, A., (2012); A novel type of silver nanoparticles and their advantages in toxicity testing in cell culture systems, *Arch Toxicol*, 86, 1089–1098

[12] Lee HY, Park HK, Lee YM, Kim K, Park SB (2007) A practical procedure for producing silver nanocoated fabric and its antibacterial evaluation for biomedical applications. *Chem Commun (Camb)* 28, 2959–2961
[13] Vigneshwaran N, Kathe AA, Varadaraian PV, Nachane RP, Balsubramanva RHJ (2007) Functional finishing of cotton fabrics using silver nanoparticles. *Nanosci Nanotechnol* 7, 1893–1897
[14] Kokura S, Handa O, Takagi T, Ishikawa T, Naito Y, Yoshikawa T (2010) Silver nanoparticles as a safe preservative for use in cosmetics. Nanomedicine 6:570–574

[15] El-Sayed, M.A., (2001); *Some interesting properties of metals confined in time and nanometer space of different shape. Acc. Chem. Res.,* **34**(4): p. 257.
[16] Biswas, A., Wang, T. and Biris, A. S. (2010), *Single metal nanoparticle spectroscopy: optical characterization of individual nanosystems for biomedical applications Nanoscale*. **2**(9), 1560.
[17] Semagina, N. and L. Kiwi-Minsker,(2009); *Recent Advances in the Liquid-Phase Synthesis of Metal Nanostructures with Controlled Shape and Size for Catalysis. Catal. Rev. Sci. Eng.*, **51**(2): p. 147.
[18] a) Ayi, A.A., Varsha Khare, V., Strauch, P., Girard, J., Katharina M. Fromm, K. M., and Taubert, T.(2010) *On the chemical synthesis of titanium nanoparticles from ionic liquids. Chem.Monthly - Monatsh. Chem.* 141, 1273–1278. b) Ayi, A. A.; Anyama, C. A.; and Etuk, S. S. (2014), Synthesis and Characterization of ZrO2 nanoparticles in ionic liquid 1-ethyl-3-methylimidazodium trifluoromethanesulfonate [EmimTfO]. *Journal of Applied Chemistry, 2 (1):26-32*
[19] Khare, V., Li, Z., Mantion, A., Ayi, A. A., Sonkaria, S., Voelkl, A., Th€unemann, A. F. and Taubert, A.(2010) Strong anion effects on gold nanoparticle formation in ionic liquids, J. Mater. Chem., 2010, 20, 1332–1339

[20] 20.Dupont, J. and J.D. Scholten, *On the structural and surface properties of transition-metal nanoparticles in ionic liquids* Chem. Soc. Rev., 2010. **39**(5): p. 1780.

[21] 21.Parnham, E.R. and R.E. Morris, *Ionothermal Synthesis of Zeolites, Metal–Organic Frameworks, and Inorganic–Organic Hybrids.* Acc. Chem. Res., 2007. **40**(10): p. 1005.
[22] Morris, R.E. (2008), *Ionic Liquids and Microwaves - Making Zeolites for Emerging Applications. Angew. Chem. Int. Ed.*, **47**(3), 443.
[23] Taubert, A.,(2005), *Inorganic materials synthesis - a bright future for ionic liquids? Acta Chim. Slov.*, **52**(3), 183.
[24] Taubert, A. and Z. Li, (2007), *Inorganic materials from ionic liquids.* Dalton Trans., **7**, 723.
[25] Li, Z., (2009), *Ionic liquids for synthesis of inorganic nanomaterials.* Curr. Op. Solid State Mater. Sci., **12**, 1.

[26] Murray C. B., Kagan, C. R. and Bawendi, M. G. (2000) Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies, *Annu. Rev. Mater. Sci.* 30:545–610
[27] La Mer VK, Dinegar RH.(1950) *J. Am.Chem. Soc.* 72, 4847–54
[28] Reiss H. (1951). *J. Chem. Phys.* 19:482
[29] De Smet Y, Deriemaeker L, Finsy R. (1997), *Langmuir* 13, 6884–88
[30] Dorjnamjin, D., Ariunaa, M., and Shim, Y. K. (2008), Synthesis of Silver Nanoparticles Using Hydroxyl Functionalized Ionic Liquids and Their Antimicrobial Activity. *Int. J. Mol. Sci. 9*, 807-820
[31] Chalmers, J. M., Dent, G., (1997). Industrial Analaysis with Vibrationalspectroscopy. Royal society of chemistry, Cambridge.
[32] Coates, J. (2000). Interpretation of infrared spectra. A practical Approach. Chichester: John Wiley and Sons Ltd Pp 10815-10837.
[33] Nakamoto
[34] Verwey, E. J. W.; Overbeek, J. T. G.(1999), *Theory of the stability of Lyophobic Colloids*, 2nd ed.; Dover, Publications: Mineola, New York, 1999. Ninham, B. W. *Adv. Colloid Interface Sci*. 83, 1.
[35] Redel, E., R. Thomann, and C. Janiak, (2008), *Use of ionic liquids (ILs) for the IL-anion size-dependent formation of Cr, Mo and W nanoparticles from metal carbonyl M(CO)6 precursors.* Chem. Commun., 1789.
[36] Redel, E., R. Thomann, and C. Janiak,(2008), *First Correlation of Nanoparticle Size-Dependent Formation with the Ionic Liquid Anion Molecular Volume.* Inorg. Chem., **47**, 14.

[37] Elechiguerra, J. L.; Burt, J. L.; Morones, J. R.; Camacho-Bragado, A.; Gao, X.; Lara, H. H.;Yacaman, M. J. (2005), Interaction of silver nanoparticles with HIV-1. *J. Nanobiotech*, *3*, 6.