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Size selective electrochemical synthesis of silver nanoparticles capped with tetra alkyl ammonium salts at various current densities

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ABSTRACT

All the physical and chemical properties are size dependent and the properties of the materials on the nanosize scale have important consequences in wide ranging fields. This paper reports the electrochemical synthesis of silver nanoparticles. The size of the synthesized nanoparticles was found to be influenced by the variation in the current density as well the nature of the tetra alkyl ammonium salts used as capping agents. Thus silver nanoparticles of varying sizes could be synthesized. These are characterized using XRD, XPS and TEM techniques.

KEYWORDS

Electrochemical synthesis;
Silver nanoparticle;
XRD;
TEM;
XPS.

INTRODUCTION

The use of silver as a bactericidal agent is in practice since ages. Its bactericidal effect has been shown against organisms like Escherichia coli and Staphylococcus aureus[1-3]. In recent years silver compounds have also been used in the treatment of burns[4]. Silver in various forms such as colloidal silver[5], nano silver coated ceramic materials[6] and nanosilver metal oxide granules[7] are also used for antibacterial applications. Due to the small size the nanoparticles exhibit novel material properties that largely differ from the bulk properties[8]. Nanoparticles of noble metals are of great interest today because of their possible applications in microelectronics[9,10], biological sensors[11] and catalysis[12]. Silver nanoparticles play an important role in the electronic industry. In recent years, with higher integrated density of the electronic components, there is a growing demand for the decrease in the thickness of the conductive films and further narrowing of the width of the printed circuit boards and the space between these circuits.

In the last few years the preparation and the characterization of nanostructured materials have become a topic of extreme interest because of their distinctive properties and potential uses in technological applications. Nanoparticles have been synthesized by a number of methods[13,14]. Of these the electrochemical reduction method[15] offers a number of advantages, namely high purity of the product, cost effective, easy experimental setup, reproducible results and size selective synthesis, which can be achieved by a variation in the current density. The process is also dependent upon the nature of the solvent[16]. The high surface energy of the nanoparticles[17,18] and consequently their tendency for agglomeration hinders their

preparation in high concentration in an aqueous system. The use of the organic solvents instead of aqueous ones might be a promising solution to this problem where the particles suffer fewer encounters between themselves due to the presence of giant hydrophobic stabilizing ligands. Moreover nanoparticles in organic media are becoming an interesting subject with a view to study optical and other phenomenon[19]. The use of tetra alkyl ammonium salts as capping agents have drawn an interest because of their labile monolayer binding properties[20] that allows post modification of the nanoparticles. Thus in the present study silver nanoparticles capped with different tetra alkyl ammonium salts and at various current density have been synthesized by the electrochemical reduction method.

EXPERIMENTAL

The reagents used in the present study were of AR grade and purchased from Qualigens (India). The sacrificial silver anode sheet and cathode platinum sheet of same sizes (1 cm x 1 cm) were 99.9% pure and purchased locally. The solvents were distilled before use. The electrolysis solution consisted of a mixture of acetonitrile and tetrahydrofuran (4:1) containing 0.01 M of tetra alkyl ammonium bromide. The different salts used were tetra ethyl ammonium (TEAB), tetra propyl ammonium (TPAB), tetra butyl ammonium (TBAB) and tetra octyl ammonium (TOAB). A 30.0 ml volume of this solution was placed in a specially designed electrolysis cell. The two electrodes were separated by 1.0 cm were dipped into the solution. The electrolysis was carried out for 2.0 hours using a current density of 6 and 10 mA/ cm^2. The product was allowed to settle overnight. The agglomerated product was then separated by decantation and washed three times with tetrahydrofuran. The product was then dried and preserved under vacuum condition. It was then characterized. The powder x-ray diffraction (XRD) pattern was obtained on X-ray powder difractometer PW 1840 using CuKα radiations ($\lambda = 1.54\ A^0$). The x-ray photo electron (XPS) studies was carried out using VG Micro Tech ESCA 3000 Electron Spectrometer at a pressure of 1.33 x 10^{-8} Pa with MgKα exciting radiations.

RESULTS AND DISCUSSION

XRD analysis

The structure of the synthesized silver nanoparticles has been investigated by x-ray diffraction (XRD) analysis. The XRD pattern of the samples prepared at various current densities and using different capping agents by the electrochemical reduction method is shown in Figure 1 and Figure 2.

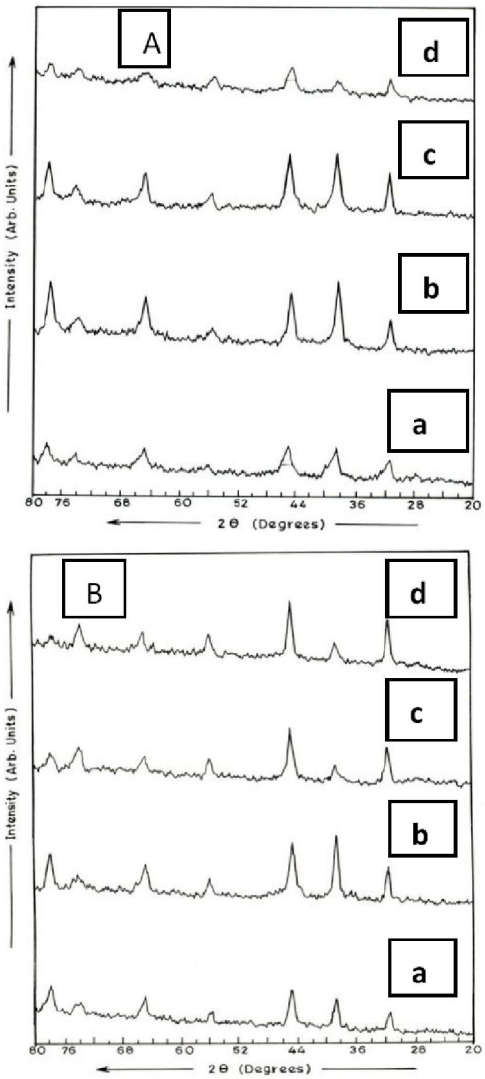

Figure 1 : XRD pattern of silver nanoparticles synthesized A) at current density of 6 mA/ cm^2, B) at current density of 10 mA/ cm^2 and a) capped with TEAB, b) capped with TPAB, c) capped with TBAB, d) capped with TOAB

For the important peaks identified from the XRD pattern, the 2θ values and the planes observed are 31.6 (111), 38.6 (111/200), 45.2 (200), 64.8 (220), 74.2 (311 and 77.0 (311). The observed 2θ values

are compared with the ASTM data. The comparison indicates the presence of a mixed phase containing silver and silver oxide with a cubic structure. The presence of the silver oxide may be due to the possible oxidation of the surface silver atoms. The average particle sizes of the samples are calculated by using the Scheerer formula and presented in TABLE 1. The average size of the silver nanoparticles is found to be in the range of 7.5 to 12.4 nm. The comparison of the average size of the nanoparticles indicates that irrespective of the capping agent it shows a decrease as the current density increases. This observation correlates well with the report[15]. The study of the particle sizes also show that as the bulkiness or the length of the alkyl group of the capping agent increases the size of the silver nanoparticles decreases.

TABLE 1 : Particle size of silver nanoparticles from XRD study

Capping agent	Average particle size (D nm)	
	At current density of 6 mA / cm^2	At current density of 10 mA / cm^2
TEAB	12.4	9.9
TPAB	11.6	9.8
TBAB	9.5	8.6
TOAB	8.6	7.5

XPS analysis

The oxidation state of the Ag in the tetra butyl ammonium capped silver nanoparticles synthesized at 10 mA/ cm^2 current density was determined by x-ray photoelectron spectroscopy analysis.

The resolved XPS spectra corresponding to O 1s is shown in Figure 3. It shows a single peak at 531.0 eV. The oxygen identified is not a part of the capping agent but may be attributed to the oxidation of the surface silver atoms by atmospheric oxygen. Such results have been reported[21,22]. The presence of O in the sample has been also observed in XRD analysis. The Figure 4 shows the resolved XPS spectra for Ag. It shows two peaks that corresponds to Ag $3d_{5/2}$ at 368.32 and Ag $3d_{3/2}$ at 374.5 eV. The observed binding energy values are in correlation with the reported[23] values for silver and silver oxide respectively. This is also indicative of the oxidation of the surface silver atoms. It is also seen there is no deviation in the observed binding energies from the standard values. This indicates that there is a weak interaction between the surface silver atoms and the capping agent, which is also stated in the report[20].

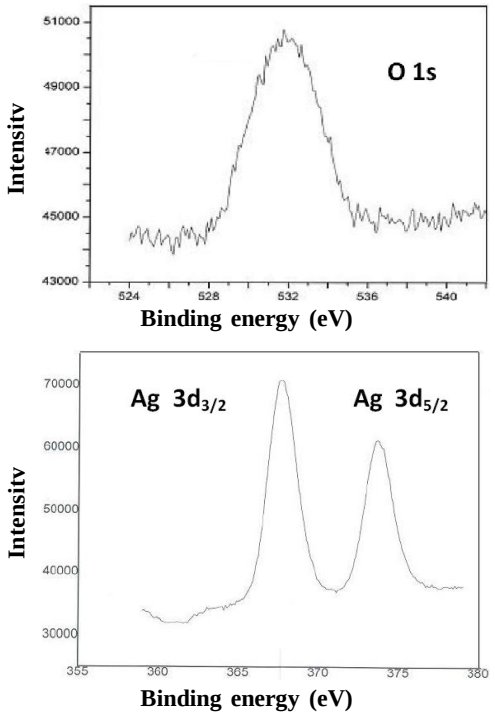

Figure 3 : XPS spectra of O 1s and Ag 3d in silver nanoparticles capped with TBAB synthesized at 10 mA /cm^2.

TEM studies

Transmission electron microscopy is a versatile

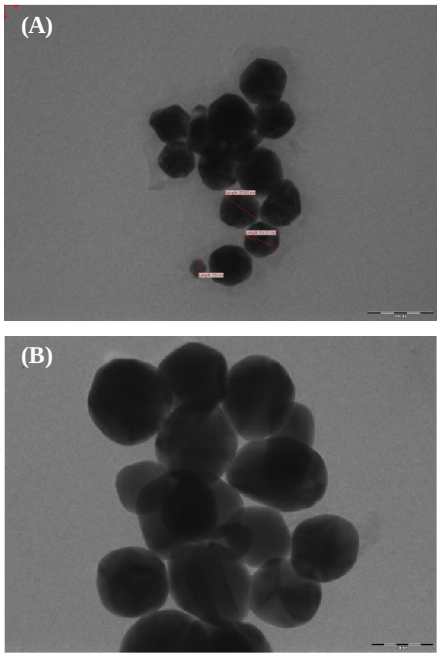

Figure 4 : 2.6.1 TEM images of Au nanoparticles capped with TEAB synthesized at A) current density of 6 mA / cm^2, B) current density of 10 mA / cm^2

TABLE 2 : Average particle size of silver nanoparticle samples obtained from TEM study

Capping agent	Average Particle size (nm)	
	At current density of 6 mA / cm^2	At current density of 10 mA / cm^2
TEAB	60.6	46.5
TPAB	35.6	28.3
TBAB	27.1	20.0.
TOAB	13.9	4.0

technique used to examine the morphology and the size of the nanoparticles. There are a number of reports[24-27] that show the use of this technique for the characterization of the silver nanoparticles. The TEM images for the silver nanoparticles capped with TEAB at 6 and 10 mA/ cm^2 is shown in Figure 5. The nanoparticles appear to be fairly spherical in shape with edges. The average particle size calculated from the TEM images for the different silver nanoparticles is shown in TABLE 1. The sizes in the TABLE 1 reflects that irrespective of the capping agent the size of the prepared silver nanoparticles decreases with the increase in the current density, a trend reported earlier[15]. It is also evident that as the bulkiness of the alkyl group in the capping agent increases the particle size of the silver nanoparticles decreases.

CONCLUSION

The results obtained from the XRD, XPS and TEM study of the silver nanoparticles capped with tetra alkyl ammonium salts synthesized at different current densities indicate, The presence of a mixed phase of silver and silver oxide in the samples. that with the increase in the current density the particle size of the sample was found to decrease. that with the increase in the bulkiness or the length of the alkyl chain the particle size of the samples decreased. There is a weak interaction between the surface silver atoms and the capping agent.

REFERENCES

[1] R.Janardhanan, M.Kareppaiah, N.Hebalkar, T.Narisinga; Polyhedron, **28**, 2522 **(2009)**.
[2] U.Klueh, V.Wanger, S.Kelly, A.Johnson, J.D.Bryers; Biomed.Mater.Res., **53**, 621 **(2000)**.
[3] G.Zhao, S.E.Stevens; Biometals, **11**, 27 **(1998)**.
[4] H.J.Klasen; Burns, **26**, 117 **(2000)**.
[5] R.Prucek, L.Kvitek; Chemica, **43**, 59 **(2004)**.
[6] S.Kawasumi, M.Yamada, M.Honma; US Patent No. 5824267, **(1998)**.
[7] J.Yan, J.Cheng; US Patent No. 6379712B1, **(2002)**.
[8] G.A.Ozin; Adv.Mater., **4**, 612 **(1992)**.
[9] G.Schimd; Chem.Rev., **92**, 1709 **(1992)**.
[10] W.A.Deheer; Rev.Med.Phys., **65**, 611 **(1993)**.
[11] M.D.Malinsky, K.L.Kelly, G.C.Schatz, R.P.Van Duyne; J.Phy.Chem.B, **105**, 2343 **(2001)**.
[12] N.R.Jana, T.K.Sau, T.Pal; J.Phy.Chem., **103**, 115 **(1999)**.
[13] M.C.Daniel, D.Astruc; Chemical Rev., **104**, 293 **(2004)**.
[14] A.Roucoux, J.Schulz, H.Palin; Chem.Rev., **102**, 3757 **(2002)**.
[15] M.T.Reetz, W.Helbig; J.Am.Chem.Soc., **116**, 7401 **(1994)**.
[16] M.Sastry; Current Science, **85(12)**, 1735 **(2003)**.
[17] D.L.Feldheim, C.A.Foss; Meta Nanoparticles, Synthesis Characterization and Application, Marcel Dekker Inc. New York, **(2002)**.
[18] S.Nath, S.K.Ghosh, T.Pal; Chem.Commun., 966 **(2004)**.
[19] K.G.Thomas, P.V.Kamath; J.Am.Chem.Soc., **122**, 2655 **(2000)**.
[20] S.R.Isaacs, E.C.Cutler, J.S.Park, T.R.Lee, Y.S.Shon; Langmuir, **21**, 5689 **(2005)**.
[21] V.G.Pol, D.N.Shrivastava, O.Palchik, M.A.Slifkin et al.; Langmuir, **18**, 3352 **(2002)**.
[22] J.C.Vickerman (Ed); Surface Analysis, The Principal Analysis Techniques, Wiley, Chinchester, **(1997)**.
[23] Handbook of Monochromatic XPS, **2**, http// www.xpsdata.com/.
[24] H.Hiramatsu, F.E.Osterloh; Chem.Mater, **16**, 2509-2511 **(2004)**.
[25] S.D.Solomon, M.Bahadory, V.Arovindan, S.A.Rufkowsky; J.Chem.Edu, **84**, 322 **(2007)**.
[26] R.Varshney, A.N.Mishra, S.Bhadouria, M.S.Gaur; J.Nanometer.and Biostructures, **4**, 249-255 **(2009)**.
[27] R.Das, S.S.Nath, D.Chadker, G.Gope, R.Bhatacharjee; J.Nanotechnology Online, 5 **(2009)**.