

Electro Chemical Synthesis of Silver Thin Film

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Abstract – The article deals a new electrochemical way of making long-lived, hanging silver nanoparticles and silver powders. There are no chemical stabilizing substances in the method. The morphology of the obtained silver nanoparticles was studied by means of electron transmission microscopy, electron microscopy scanner, atomic microscopy and dynamic light dispersal measurement. The creation of silver crystalline structures consisting of agglomerating silver nanoparticles on cathode surface during the electrochemical procedure was shown. Silver nanoparticles have diffuse reflective spectroscopy characterized their optical properties. From the diffuse reflection using Kubelka – Munk formula, the optical band gap energy was determined for the electrodeposited AGNPs. The crystalline character of silver nanoparticles confirmed the growth of nano silver crystals in X-ray (XRD) studies. The XRD design showed that the electrodeposited Ag NPs had a dendrite dominance in the cubic geometry. Debye–Scherrer equation was considered for the average particle size and peak expansion, while Williamson–Hall method was used to study the peak expansion strain. A high-resolution microscope of scan of electrons characterized the surface morphology of the Ag NP and results showed a high degree of particle aggregation. The antifungal activity of Ag NPs was assessed and demonstrated an unprecedented level of antibacterial activity in combination with streptomycin against multi-drug resistant strains like *Staphylococcus aureus*, *Bacillus subtilis*, *Klebsiella Pnumonia* and *Escherichia coli*.

Key Words – Silver, Nanoparticle, PVP, Electrochemical Synthesis, Colloids, Antibacterial Activity, Silver Nano Dendrite.

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INTRODUCTION

During the last decade the synthesis and characterization of nanoparticles and their powders were carried out using different methods (Feldheim and Foss 2002). Nanoparticles find their way into different fields in science and technology, due to their different properties than bulk metal (Mazzola, 2003; Anselmann, 2001; Bo`hemann and Richards, 2001; Biswas and Wu, 2005). The wide variety of possible applications, including medicine (Salata 2004), catalysis (Lewis 1993), textile engineering (Lee and Jeong 2005) biotechnology and bioengineering (Niemeyer 2001), water treatment (Solov'ev et al. 2007), electricity (li et al. 2005) and optics, have particularly drawn attention to silver nanoparticles (Murphy et al. 2005). Much approaches have been developed for game irradiation (Long et al. 2007), electron irradiation (Bugle et al. 2006), chemical reductions by inorganic and organic reduction substances (Bo nemann and Richards 2001), photochemical (Mallick et al. 2003), microwave processing (Yin et al. 2004), and thermic reduction agents (Bo`hemann and Richards 2001). A variety of approaches were developed for obtaining silver Nanoparticles of various shapes and dimensions (Navaladian et al. 2007). The first techniques for the

electro-chemical synthesis of nanoparticles were described by Reetz and Helbig in detail (1994) where a metal sheet was dissolved anodically and intermediate metal salt formed at the cathode was reduced to produce the metal part of which stabilized by salts of tetraalkylammonium. The study was successfully adopted in electrochemical synthesizing silver acetonitrile nanoparticles containing Rodri'guez-Sa'nchez et al tetrabutylammonium salts (2000). Silver nanoparticles were obtained from Starowicz et al., 2006, by means of the similar method, by potentiostatic or galvanostatic silver polarisation. In the processes of electrochemical synthesis of silver particles, Poly(N-vinyl-2-pyrrolidone) was essential in Yin et Al(2003). 's Electrochemical methods have main advantages in terms of the high purity of particles and the ability to adjust the current density with nanoparticles without the need for expensive devices or vacuums. The right choice of chemical agents and process conditions are the key to the success of electrochemical methods. The method has its limitations however, as noted above (Rodri Guez Sa'nchez et al. 2000, as the effective surface available to particle production diminishes by the deposition of silver on the cathode during electrochemical processes. The production of

particles stops entirely as the whole cathode surface is covered by silver electrodeposits. In the current search for simpler and more economic methods of nanoparticle synthesis, it is also important to find ways of avoiding the use of stabilization materials in electrochemical processes. In this article, we present a new electrochemical approach for the production, without chemical stabilizing agents in long-lasting silver-nanoparticles hanging on water solutions as well as silver powders placed on electrodes.

MATERIALS AND METHODS

A cheap two-electrode setup in which the anode and cathode are made from Ag bulk, to be turned into colloidal particles is the basis of the proposed procedure for obtaining silver nanoparticles. As an anode and a cathode we used two polished silver plates with a face-to-face distance of 10 mm (85 mm 9 20 mm 9 4 mm). The electrodes were dipped in a 500 mL distilled water electrochemical cell from an ordinary commercially available water distillery (DE-25, Russia). In the temperature range 20–95 °C, electrolysis was conducted at constant tension of 20 V. The polarity of direct current between electrodes every 30–300 s, and intense riveting during the electrical process, are additional technological keys to the electrochemical synthesis of silver nanoparticles, which inhibit the formation of precipitates. The silver nanoparticle solutions thus produced have been stored in glass containers under environmental conditions. Neutron activation analysis determined the concentration of silver nanoparticles in solutions (Soete et al. 1972). The samples were irradiated in the Institute of Nuclear Physics' nuclear reactor (Tashkent, Uzbekistan). The product of the $^{109}\text{Ag}(n,\gamma)^{110m}\text{Ag}$ nuclear reaction is half-life $T_{1/2} = 253$ days. Measures of the gamma radiation intensity of 0.657 MeV and 0.884 MeV emitted at ^{110m}Ag were used to establish the silver concentration. For gamma ray quanta recording use was made of a Ge(Li) detector with a resolution of approximately 1.9 keV at 1.33 MeV and a 6144 channel analyzer. A Zetasizer (ZEN3600, Malvern Instruments, UK) was used to estimate the distribution of silver nanoparticles in solutions at 25 °C in dynamic light scattering (DLS). The silver powder morphology deposited on the cathode surface during the electrochemicals were observed by electron microscopy of field emission scanning (FE-SEM; JSM-6700F, JEOL, Japan). The size and form of the solution's nanoparticles was determined by electron transmission microscopy (TEM) (LEO-912-OMEGA, Carl Zeiss, Germany). For the determination of the chemical composition of the samples, the energy dispersive X Ray (EDS) spectrometer attached to the TEM was used. The average size values for different TEM micrograms in a single sample were over 150 nanoparticles. In addition, silver nanoparticles suspended into aqueous solutions were photographed with the use of freshly-cut mica surfaces as substrates as atomic force microscopy (AFM) (Solver P47Bio, NT-MDT Co., Russia).

RESULTS AND DISCUSSION

Unlike the most non-electrochemical methods, the proposed electrochemical synthesis approach does not require the use of sophisticated vacuum cameras, or expensive equipment.

Stage I: formation of a colloidal solution of silver nanoparticles

This stage comprises the following steps (Fig. 1):

1. Oxidative dissolution of the sacrificial Ag anode:

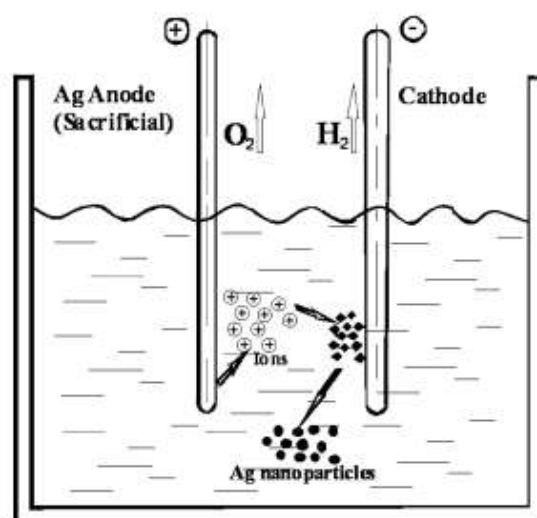
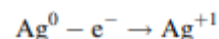


Fig. 1 Electrochemical formation of silver nanoparticles in distilled water

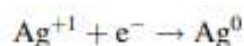


2. Release of the oxygen gas:

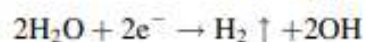


due to the electrolysis of water, with simultaneous Ag_2O film deposition on the surface of the anode;

3. Ag^+ ions migration to the cathode;
4. Reductive formation of zero-valent Ag atoms on the cathode:



and release of the hydrogen gas:



5. Formation of silver nanoparticles via nucleation and growth due to attractive van der Waals forces between Ag atoms;

6. The separation and further migration of synthesized silver nanoparticles caused by the vigorous agitation of a solution.

When the voltage is used, the above-mentioned reactions and the electric current are continuously increased until the saturation level is reached. The hotter the water, the quicker the response, the higher the saturation value (cf Fig. 2). The polarity of the direct current between electrodes changed periodically during the first described phase of electro-chemical synthesis, reducing silver electrodependence on the cathode significantly. Once the polarity changes, Ag₂O begins to decrease with hydrogen on the surface of the previous cathode

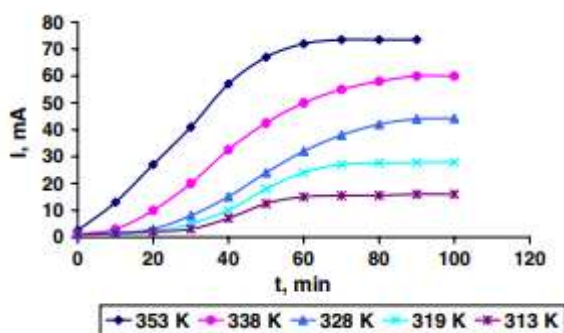
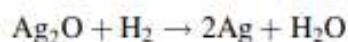


Fig. 2 Current versus process time for different temperatures



at temperatures above 50 C. We have changed the time span of the polarity between 30 and 300 s. Empirically, it was found that 4 minutes was a best time. At the cost of a silver film deposition at the cathode, agglomerations of particles were improved at smaller values in the solution. For values of more than 4 minutes, the effective surface for particulate production was gradually decreased due to significant growth in the position of silver electrodes on the cathode. By changing the polarity periodically every 4 minutes, the film deposition on the electrodes was reduced as opposed to known electrochemical methods and the production of nanoparticles increased and the silver colloids increased.

HR-SEM

Structural morphology of Ag NPs was characterised by FEI Quanta FEG 200 electron microscope. Figure 3 shows the HR-SEM images of the well-dispersed Ag NDs synthesised at room temperature. HR-SEM results showed that the Ag NPs obtained by the electrochemical synthesis are pure in nature and dendritic in shape, with the size 10–50 nm and are in good agreement with the XRD analysis.

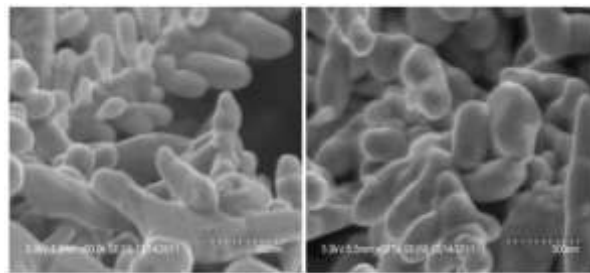


Fig. 3 FE-SEM micrographs of Ag NDs

X-RAY DIFFRACTION ANALYSIS

In the Seifert Analysis X-ray diffractometer, Cu Ka radiation was used between 108 and 708 to examine the crystalline structure of the synthesized Ag NPs, and this can be seen in fig. 4. XRD analyzes have shown that Ag np are very crystalline and of face-centered geometry (FCC). The pattern of the XRD showed peak diffraction of 2θ values of 38.16, 44.35 and 64.47, which corresponded to the reflections of Bragg (111), (200) and (220). The XRD pattern was more preferred at 2θ = 38.16, which reflects (111) the NDs of the Ag. That was well in keeping with the unit cell of the facial-centric cubic (fcc) structures (JCPDS file No. 04-0783).

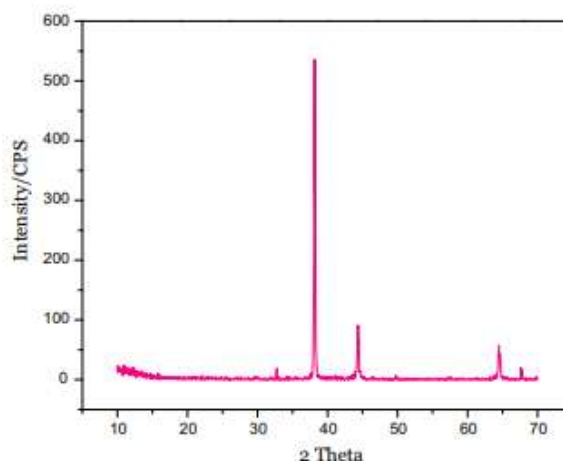


Fig. 4 XRD pattern of the electrodeposited Ag NPs

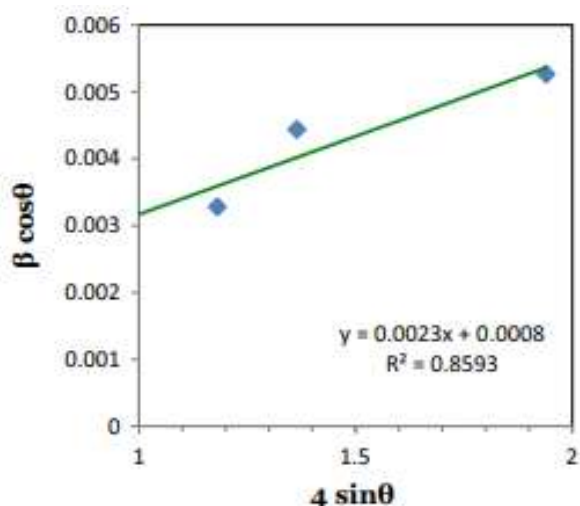


Fig. 5 Williamson–Hall analysis of silver Nano dendrites. Fit to the data, strain is determined from the slope and crystalline size from the intercept of the fit

CONCLUSION

The electro-mining of anodically solved silver nanoparticles in water has been studied in silver nanoparticles obtained through a three-step process. Different technological keys have been considered to improve the output by changing process conditions. DLS, TEM and SEM measurements were employed to study the morphology of colloidal silver nanoparticles and powders placed on electrodes. These studies show that nanoparticles of silver suspended in the water solution produced by the present three-stage technique were almost spherical with an average size of 7.3 ± 3.1 nm. Measuring AFM was shown to be stable enough for at least 7 years, even under ambient conditions, for silver nanoparticles that were synthesized using the proposed method. Moreover, small additional PVPs have been shown to enhance their stability with respect to silver nanoparticle solutions. The effect, however, is not very pronounced and this is not a crucial step. Research of silver particles on the cathode surface during the electrochemical process revealed that the silver powders obtained were 'bi-modal': large polyhedron-formed micron-fitting particles and silver-fitted plates consisting of agglomerated silver nanoparticles up to 40 nm in size. In applications requiring silver powders with a broad surface, this 'by-product' of electrolysis can also be used. The simplicity of this route of synthesis makes large quantities of silver nanoparticles low-cost. There is generally no need for chemical stabilization agents that increase the technological viability of the method and the industrial applications. We feel that the electrochemical method presented for synthesizing silver nanoparticles provides an efficient way of manufacture of colloidal solutions in the range of 20 to 40 mg/L silver or Nano particulate matter in the case of silver nanoparticles.

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