ELECTROCHEMICAL SYNTHESIS OF SILVER NANOPARTICLES IN AQUEOUS ELECTROLYTES

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The paper reports studies about electrochemical synthesis of colloidal silver solutions involving the so-called "sacrificial anode" technique. Poly (N-vinyl-2-pyrrolidone) (PVP) and sodium lauryl sulfate (Na-LS) have been used as a stabilizer and co-stabilizer, respectively. The recorded UV/Vis spectra evidenced the presence of absorption band centered at 420 nm, which is characteristic for Ag nanoparticles presence in the colloidal system. Based on DLS measurements and TEM micrographs, the conditions for preparing stable and high purity nano-Ag based colloidal solutions containing 40-60 ppm Ag particles with size around 10-20 nm has been established. The zeta potential distribution in a monomodal manner, with potential values between -17 mV and -30 mV, suggests the existence of particles covered by stabilizer and, therefore, a stable colloidal system.

Keywords: silver nanoparticles, electrosynthesis of nanoparticles, colloids, nanotechnology

1. Introduction

In the last three decades, the interest in the synthesis and application of metal nanoparticles has significantly increased, due to their new and different characteristics as compared with those of macroscopic phase. Nanoparticles allow attractive applications in various fields, such as: medicine, biotechnology, optics, microelectronics, catalysis, storage of information, energy conversion [1]. Silver nanoparticles display unique properties normally associated with the noble metals (chemical stability, excellent electrical conductivity, catalytic activity), along with other more specific ones (antibacteriostatic effects, nonlinear optical behavior,

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etc.), while still being reasonably priced. Moreover, nano-silver based colloidal solutions are particularly involved in environmental and biological applications due to their specific antimicrobial properties, against a great number of bacteria and fungi.

The nanoparticles shape and size greatly affect the metals properties on the nanometre scale [2] and it is therefore critical to develop an effective method to prepare nanoparticles with well controlled shape and size. Small metal particles are usually obtained by chemical reduction of metal salts; their sizes vary as a function of the involved stabilizer, reducing agent as well as solution concentration, temperature, solvent or synthesis time. Several methods of producing metallic nanoparticles, including silver ones were reported in refs. [3-6]. Among electrochemical techniques, the conventional DC electroplating (under galvanostatic or potentiostatic control) or pulsed-current deposition are attractive routes to synthesize nanocrystals of pure metals, alloys, and metal matrix composites. They proved to have some additional advantages regarding preparation of size-selective or shape-controlled metal nanoparticles and also allow high productivity [7-10].

Reetz and Helbig [11] reported for the first time the electrochemical synthesis of metallic nanoparticles involving tetraalkyl-ammonium salts as stabilizing agents. Using the same approach, Rodriguez–Sanchez *et al.* prepared silver nanoparticles in acetonitrile containing tetrabutyl-ammonium salts [12] and Yin *et al.* [13] discussed the role of poly (*N*-vinyl-2-pyrrolidone) (PVP) as a stabilizer for the obtained silver clusters. Their results showed that the rate of transfer of PVP-stabilized silver clusters from the cathodic vicinity to the bulk solution played an important role in preparation of the monodispersed nanoparticles. Usually PVP is mostly used as stabilizer agent, controlling the particles shape and size in electrochemical [14] and also in chemical [15,16] syntesis procedures. The formation of Ag nanocubes [17] and nanowires [18] have been reported, too. The addition of sodium lauryl sulfate (Na-LS) as co-stabilizer usually ensure the wrapping and electrostatic stability of the silver nanoparticles in solutions.

With this in view, the present paper presents some experimental results dealing with electrochemical synthesis and characterization of silver nanoparticles obtained in the presence of a mixture of stabilizers and co-stabilizers agents, including PVP [poly (N-vinylpyrrolidone)] with a molecular weight of 55000, and Na-lauryl sulphate (Na-LS), respectively. The novelty of this so-called "sacrificial anode" method [19] consists in the use of a mixture of ionic and non-ionic biocompatible surfactants in order to stabilize the colloidal system. Cyclic voltammetry has been employed to investigate the influence of the above mentioned stabilizers on silver particle dimensions.

2. Experimental

2.1 Synthesis of colloidal silver solutions

The electrosynthesis of silver nanoparticles (AgNPs) by "sacrificial anode" method was performed with a home-built current pulse generator with alternating polarity and a stirrer. There have been used Ag electrodes of 99.999% purity with sizes of 105×30 mm, immersed in deionised water as dispersing medium (its electrical conductivity being lower than 1 μScm^{-1}). The working parameters during formation of silver colloidal solution were: 5-10 mA for the applied direct current and 3-7 hours for the processing time. PVP with a molecular weight of 55000 as a non-ionic stabilizer (symbolized PVP 55) and Na-lauryl sulphate (Na-LS) as ionic stabilizer have been purchased from Aldrich and used as received. The obtained AgNPs colloidal systems have been stored under dark conditions.

2.2 Characterization of silver colloidal solutions

Cyclic voltammetry (CV) has been applied to get more information on the influence of PVP concentration on electrochemical reduction of silver ions. An Autolab PGSTAT 12 EcoChemie electrochemical system driven by PC was used. The electrochemical cell contained a Pt working electrode with a geometrical surface of 0.03 mm^2, an Ag wire as quasireference electrode and a Pt mesh as auxiliary electrode. The applied scan rates were in the range 50-250 mVs^{-1}. Solutions of 5 mM $AgNO_3$ and 0.1 M KNO_3 with various concentrations of PVP 55 stabilizer have been used as electrolytes. Before each CV measurement, the surface of Pt working electrode was cleaned to remove reductive substances by polishing with 50 μm alumina paste, rinsing with HNO_3:H_2O 1:1 solution and washing with water. All experiments have been performed in stationary conditions at room temperature (20±5^oC). The silver concentration of the obtained colloidal solutions has been determined by quantitative analysis using atomic absorption spectroscopy (NovAA 330 SA equipment) and UV-VIS absorbance spectra recording involving a JASCO V 500 spectrophotometer.

The nanoparticle sizes and *zeta* potential have been determined through QELS (Quasi Elastic Light Scattering) technique using a Nano-sizer Brookhaven BI-MAS type equipment. Zeta potential indicates the colloidal silver solution stability and it has been measured by Laser Doppler Velocimetry procedure. Values of zeta potential below -30 mV and above +30mV indicate stable solutions [20]. The silver nanoparticles morphology and dispersibility were evidenced by transmission electron microscopy (TEM), using a Philips CM 100 microscope. The specimens for TEM investigations have been prepared through deposition on 400 mesh grids with formvar film.

3. Results and discussions

To get more information on the electrochemical process during electrosynthesis of Ag NPs, as well as on the role and optimum concentration of stabilizers, cyclic voltammetry measurements were carried out. In the stabilizers-free electrolytic solutions, silver ions were rapidly electrodeposited on the platinum cathode, after the electrolysis process began. Fig. 1 shows comparative examples of recorded voltammograms with and without PVP addition in a $AgNO_3$ based electrolyte. The cathodic peak assigned to Ag reduction is evidenced at potentials around -0.22 V in the PVP-free solution, with a very slight displacement towards -0.20 V in the presence of PVP. The cathodic peak current has a quite equal magnitude, regardless the electrolyte composition.

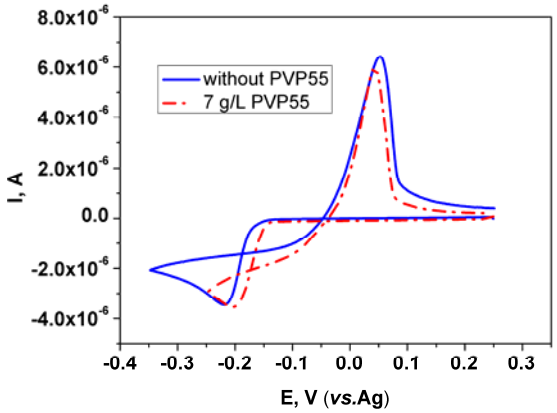

Fig. 1. Cyclic voltammograms for the redox processes of silver ionic species in 5 mM $AgNO_3$ + 0.1 M KNO_3 solution, without and with PVP 55 (7 gL^{-1}).
S_{WE}= 0.03 mm^2, scan rate 100 mVs^{-1}

The electrochemical reduction of the silver ions involves two cathode surface processes, respectively the formation/nucleation of silver particles onto the cathode surface and the deposition of silver layer. The addition of PVP facilitates the particle formation rate and reduces the silver film deposition rate [12]. The anodic peak corresponding to Ag dissolution appears at potentials around +0.05 V/Ag ref. in the PVP free solution with a shift towards +0.04 V/Ag in the presence of PVP. The anodic peak current in the absence of PVP is relatively higher than that evidenced in the presence of PVP. It can be assumed that in the PVP free solution the entire amount of electroreduced silver has been completely dissolved to form Ag (I) ionic species, while in the PVP containing solution, just the electrodeposited silver (Ag film on the cathode) has been again dissolved during anodic sweep. In the presence of PVP, anodic dissolution current is lower, thus also proving that a part of metallic silver remains in the

solution, as nanoparticles protected by the stabilizer. This behavior is in a good agreement with the findings [16] that silver ions are directly reduced to silver nanoparticles stabilized by PVP, without any oxidation side reaction during the process.

To get more information on the optimum PVP content in the electrolyte used in silver nanoparticles electrosynthesis, cyclic voltammograms have been recorded at different PVP 55 concentrations and a constant addition of 0.5 gL^{-1} Na-lauryl sulphate for 10 cycles, as exemplified in Fig. 2.

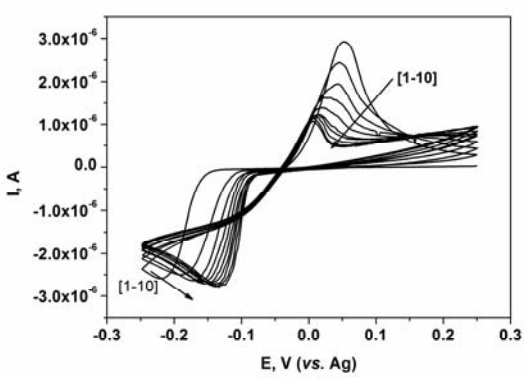

Fig. 2. Cyclic voltammograms for 5 mM $AgNO_3$ + 0.1 M KNO_3 system containing 7 gL^{-1} PVP 55. S_{WE} = 0.03 mm^2, scan rate 50mVs^{-1}

According to Fig. 2, the anodic peak current significantly decreased with cycle number, thus proving the increase of silver content in the solution as nanoparticles and a significant decrease of the electrodeposited one. The dependencies of anodic peak current values against the cycle number were plotted for different PVP 55 concentrations in the electrolyte, as illustrated in **Error! Reference source not found.**, where the voltammograms were recorded at100 mVs^{-1}.

In all CV curves the anodic peak current decreased with the increase of the cycle's number. The major decrease is evidenced in the case of 7 gL^{-1} PVP 55 concentrations. Considering this diminution of anodic peak current as an evidence of increasing Ag nanoparticles electrosynthesis rate, one may thus suggest that the optimum content of PVP 55 allowing a suitable formation of Ag nanoparticles should be around 7 gL^{-1}.

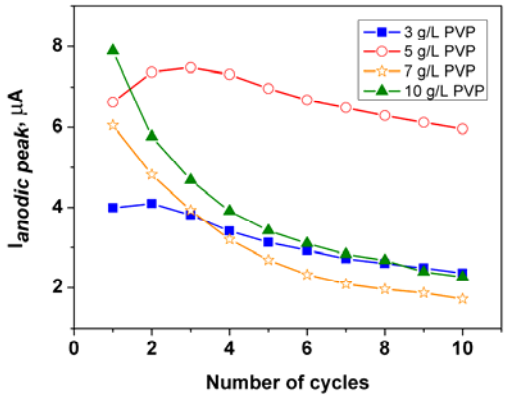

Fig. 3. Dependence of anodic peak current *vs.* number of CV cycles for different values of PVP 55 concentration. S_{WE} = 0.03 mm^2, scan rate 100 mVs^{-1}

Based on recorded cyclic voltammograms, the optimum concentrations of stabilizers and co-stabilizers may be estimated and further be involved to synthesize AgNPs applying the "sacrificial anode" method.

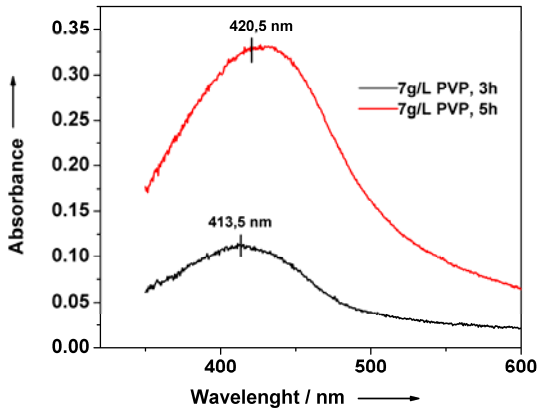

Fig. 4. UV/Vis absorption spectra of AgNPs colloidal solutions electrosynthesized in electrolytes containing 7gL^{-1} PVP55 for two process time durations, 3h and 5h

UV/Vis absorption spectra for the electrosynthesized AgNPs colloidal solutions have been also recorded for two process time durations, as exemplified in Fig. 4. A broad absorption band centred at around 420 nm is evidenced, which is characteristic to the presence of metallic silver. This is usually assigned to the surface plasmon excitation of silver particles [17-19,21-24]. The longer time duration of the process, the smaller probability to obtain ultrafine silver particles by electrochemical synthesis is; therefore, a slower transfer rate of the silver ions

towards the cathode. A decrease in the particle size induces a decrease in the plasmon band intensity [23,24].

By adding Na-LS as ionic stabilizer, the distribution of metallic nanoparticles size is improved due to the association between the ionic stabilizer and the PVP.[25].This behavior is characteristic for a slow formation rate of silver particles. The PVP molecules adsorb on the surface of silver particles. The concentration of silver particles increases once the electrolysis proceeds. This is also shown by the change in colour of the solution, from the light yellow at the beginning of the process to brown colour at the end of the process.

The presence of co-stabilizer facilitates a higher content of AgNPs in the obtained colloidal systems, as Table 1 illustrates. Na-LS stabilizer has amphiphilic properties due to the C12 chain (lipophilic) attached to sulphate or sulphonate group (hydrophilic). This bifunctionality in one molecule provides the basic properties useful in the steric and electrostatic stabilization of silver nanoparticles [26].

Table 1

AgNPs concentration in colloidal solutions against stabilizer mixture (electrochemical synthesis period of 5 h)

Composition of electroformation solution	Concentration (ppm)
5 gL^{-1} PVP 55	46.65
5 gL^{-1} PVP 55 + 0.25 gL^{-1} Na-LS	49.20
5 gL^{-1} PVP 55 + 0.5 gL^{-1} Na-LS	56.71
5 gL^{-1} PVP 55 + 0.75 gL^{-1} Na-LS	58.10
5 gL^{-1} PVP 55 + 1 gL^{-1} Na-LS	61.55

To analyse the nanoparticles size, their granulometric distribution has been recorded. A typical sample of AgNPs colloidal solution contains however a certain amount of large Ag colloidal particles after electrosynthesis, as illustrated in Fig. 5. Usually, the size of the particles is between 10 nm and 55 nm. In order to remove the larger colloidal particles, the AgNPs colloidal systems have been subjected to a centrifugation step for 15 min. at 5000 rotations/min. Thus, a 10-15% supplementary decrease of the Ag content in the final solution was evidenced, too.

The stability of obtained colloidal solutions has been determined by measurements of electrokinetic potential (*zeta* potential). The *zeta* potential indicates if the particles present in a liquid medium tends to associate or sediment. For the electrochemically synthesized AgNPs colloidal solutions, values of zeta potential between -17 mV and -35 mV have been measured, suggesting a suitable stability, however with a slight tendency of agglomeration. Fig. 6 presents an example of the recorded diagram regarding zeta potential for AgNPs colloidal solutions, electrochemically synthesized in the presence of 5 gL^{-1} PVP 55 + 0.5

gL^{-1} Na-LS for 5 h (three succesive measurements are represented, showing an adequate reproducibility). This behavior suggests that the colloidal particles are covered with stabilizer agent and thus the solution is stable [27].

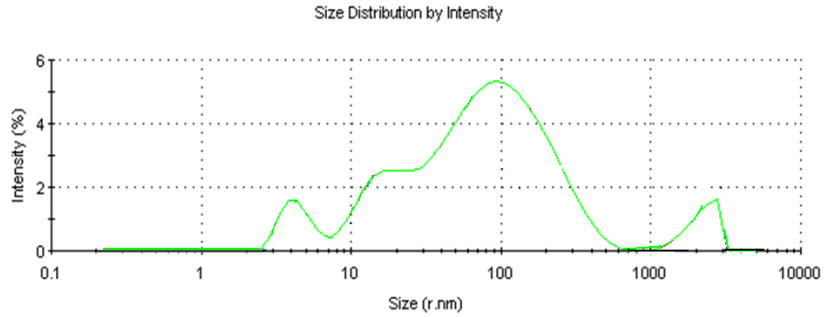

Fig. 5. Typical DLS-images of size distribution by intensity of silver nanoparticles electrochemically obtained in solutions containing 5 gL^{-1} PVP 55 + 0.5 gL^{-1} Na-LS (56.71 ppm Ag)

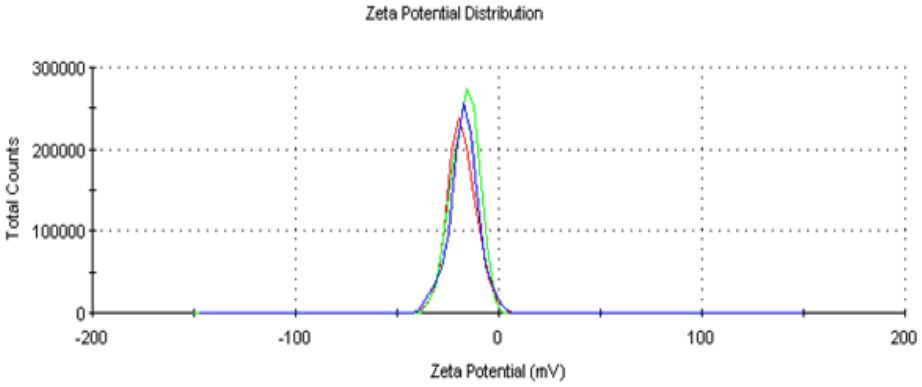

Fig. 6. Granulometric distribution of particles against zeta potential for a colloidal solution containing Ag, formed in the presence of 5 gL^{-1} PVP + 0.5 gL^{-1} Na-LS, 5h

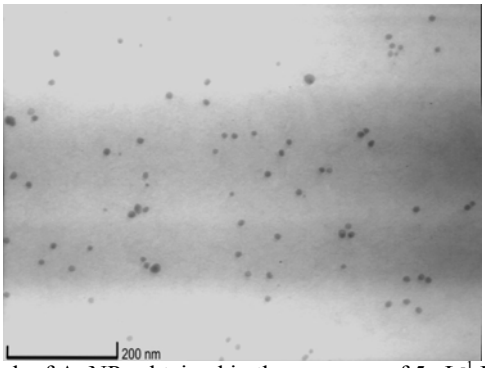

Fig. 7. TEM micrograph of AgNPs obtained in the presence of 5 gL^{-1} PVP + 0.5 gL^{-1} Na-LS

(5h process duration)

Fig. 7 illustrates an example of TEM micrograph for the electrochemically synthesized AgNPs in the presence of PVP 55 and Na-LS. The nanoparticles show a spherical shape, having sizes in the range 18-25 nm.

4. Conclusions

High purity nano-Ag based colloidal solutions have been successfully electrochemically synthesized, based on the so-called "sacrificial anode" technique. The use of PVP stabilizer associated with Na-lauryl sulphate co-stabilizer facilitated an adequate dispersion of the formed silver nanoparticles and hindered their agglomeration. Moreover, their addition increased the rate of nanoparticles formation, so that nano-colloidal solutions containing 40-60 ppm Ag have been obtained for process time durations up to 5 h.

It was demonstrated that cyclic voltammetry proves to be a useful tool to evaluate the optimum content of stabilizer/co-stabilizer through analysis of the anode current peak values against the cycle's number, as an indicator of the colloidal nano-Ag amount formed into the solution. Also, the recorded UV/Vis spectra evidenced the presence of absorption band centred at 420 nm, characteristic to Ag nanoparticles presence in a colloidal solution.

DLS measurements and TEM micrographs showed the formation of Ag spherical nanoparticles having sizes around 10-55 nm. The zeta potential values between -17 mV and -35 mV suggest a suitable stability, however with a slight tendency of agglomeration.

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