Stable colloidal silver solutions for different applications

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The paper presents a method for obtaining of some stable colloidal silver solutions containing 5…100 ppm silver nanoparticles. This method is based on the reduction of aqueous silver nitrate solutions with sodium borohydride solutions in presence of a steric stabilizing agent (PVP) and an electrostatic stabilizing agent (tri-sodium citrate), being in certain molar ratio. We obtained by this method some high defined colloidal silver solutions having spherical silver nanoparticles with a narrow grain size distribution, depending on the colloidal silver solutions concentrations. The grain size and the shape of the particles were studied by TEM. The mean diameter of the silver nanoparticles, the grain size distribution and the zeta potential were measured by DLS on a nanoparticles size analyzer. The colloidal silver solutions stability was assessed monthly by zeta potential and UV-Vis spectra recording for a time period of six months. The zeta potential of the studied colloidal silver solutions was included in the range of – 44.82 mV and - 31.88 mV. These values proved a high stability of the solutions.

1. Introduction

Over the past decade, the stable colloidal silver solutions (CSSs) present a great interest due to their properties such as antimicrobial activity, high electrical and thermal conductivity, catalytic activity or unique optical properties that depend on the size and the shape of the particles.

The success of the introduction of the silver nanoparticles (SNPs) in different forms in bioscience, healthcare and consumer goods is well known [1 – 7].

However, the CSSs are unstable and are subjected to the irreversible aggregation and oxidation, especially when the SNPs have a high concentration.

By SNPs covering with an organic or inorganic layer, the stability and self assembling ability of the particles can be improved [8 – 14].

The frequently methods used for CSSs preparing are chemical and electrochemical ones. But, these methods have limitations in controlling of the particle size, colloidal stabilities, production on industrial scale and dispensability, especially.

To overcome these limitations some surfactants have been used in order to avoid the particle agglomeration and to achieve a stabilization of the CSSs [9 - 11].

The concentration of solutions, reaction rate and nature of the stabilizing agents are very important parameters in the achievement of the proper characteristics of the final CSSs, such as: grain size, shape, uniformity of distribution of the SNPs and stability.

In this paper we present a chemical method for reduction of Ag^+ ions to Ag^0 nanoparticles, in aqueous solutions, for obtaining some stable CSSs, consisting of monolayer-protected SNPs in different concentrations.

2. Experimental

The experiments were carried out using the following starting materials:

- deionized water with conductivity $< 1 \mu S/cm$;
- silver nitrate aqueous solutions of 0.017…0.085 wt. % concentrations ($AgNO_3$, p.a., crystallized, ≥ 99.9 % of Fluka);
- tri-sodium citrate solutions of 0.5…2 wt. % concentrations ($C_6H_5Na_3O_7 \cdot 2H_2O$, 99…101 % of Merck);
- poly [1-vinyl-2-pyrrolidone] $(C_6H_9NO)_x$ solutions of 0.5…0.7 wt. % concentration (PVP10 with M = 10,000 of Sigma – Aldrich);
- sodium borohydride solutions of 0.075…0.15 wt. % concentrations ($NaBH_4 \geq 96$ % of Merck).

In order to obtain some stable CSSs with high defined SNPs we used the reduction method of Ag^+ ions from an $AgNO_3$ aqueous solution by sodium citrate and sodium borohydride in proper conditions relating to concentration, temperature, pH, food rate and stirring [14]. The tri-sodium citrate is both a reductive agent and an electrostatic stabilizer for SNPs. Also we used a PVP solution as a steric stabilizer.

The tri-sodium citrate solution was dropped in the aqueous solution of $AgNO_3$ and PVP which was heated at 70…90 °C and energically stirred. After a light yellow color appeared, the suspension was rapidly cooled and kept at 4 °C. Then, the $NaBH_4$ solution was dropped in a $NaBH_4:AgNO_3$ molar ratio of 1:1 …1:2. The final pH of solution had the value of 9.

The CSSs were characterized from grain shape and sizes, dimensional distribution of the grains, zeta potential and UV-vis absorbance. For this purpose, we used a nanoparticles size analyzer of Brookhaven 90 Plus type for

the measurements of SNPs mean diameter, grain size distribution and zeta potential, a Philips microscope of CM100 type for TEM analyses and a spectrophotometer Able & Jasco of V-570 type for the measurements in UV-VIS of absorbance spectra and determination of SNPs concentration in CSSs.

3. Results and discussion

Based on the presented method, we obtained some CSSs with SNPs content ranging between 5…100 ppm, according to the results achieved by UV-Vis spectrophotometer methods. The UV-Vis analyses are facile ways for some qualitative and quantitative assessments of SNPs solutions. The optical absorbance spectra feature of SNPs solutions depend strongly on the SNPs properties (size, shape and concentration) and the environment in which the SNPs are dispersed. It is a result of frequency changes at which conduction electrons oscillate in response to the alternating electric field of incident electromagnetic radiation. This phenomenon observed in visible spectrum is known as surface plasmon resonance (SPR), and gives rise of some intense colors specifically only for metals with free electrons (essentially Au, Ag Cu and alkali metals). So, the SNPs obtained solutions present colors changing from light yellow to dark brown. The appearance of a light yellow color during synthesis marks the SNPs solution formation with concentrations of a few ppm.

Fig. 1 presents the UV-Vis absorbance spectra of some CSSs with different concentrations of SNPs, ranging between 5…100 ppm.
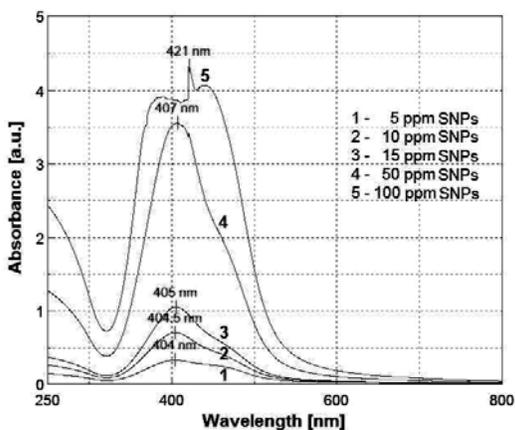

Fig. 1. UV-VIS absorbance spectra of some CSSs with different concentrations of SNPs

The absorbance in UV-VIS spectrum (Fig. 1) of the CSSs with SNPs concentrations between 5…50 ppm occured at $\lambda = 404...407$ nm. For SNPs concentrations between 50…100 ppm, the peak of SPR begin to splint and shift to higher wavelengths with concentration increasing. At SNPs concentrations greater than 50 ppm, the particles sizes are greater. In this case, the rate growing and the agglomeration tendency of SNPs are more increased comparatively with dilute solutions.

Figs. 2-4 present the TEM images of SNPs from some CSSs with concentrations of 15 ppm, 50 ppm and 100 ppm respectively. The visible split of the UV-VIS spectra, starting from concentrations of 50 ppm SNPs (Fig. 1) shows the existence of some particles that changed the spherical shape into elongated shape as we can see in Fig. 4. The elongated nanoparticles display two distinct plasmon bands related to transverse and longitudinal electron oscillations. The longitudinal oscillation is influenced by aspect ratio of SNPs and little deviations from spherical geometry can lead to impressive shift of the SPR peak and color changing, respectively [2].
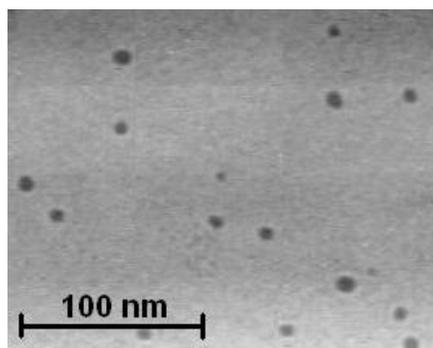

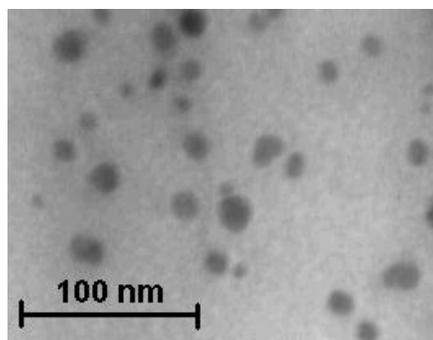*Fig. 2. TEM micrography of a CSS with a SNPs content of 15 ppm.*

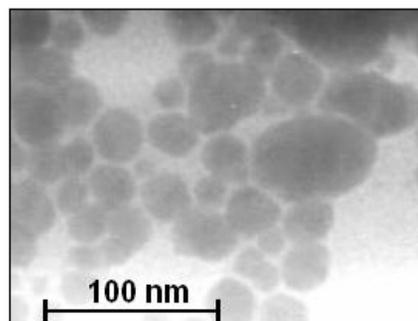*Fig. 3. TEM micrography of a CSS with a SNPs content of 50 ppm.*

Fig. 4. TEM micrography of a CSS with a SNPs content of 100 ppm.

In Figs. 5-7 are presented the grain size distributions of

the SNPs from solutions having concentrations of 15, 50 and 100 ppm, recorded by dynamic light scattering (DLS) method.
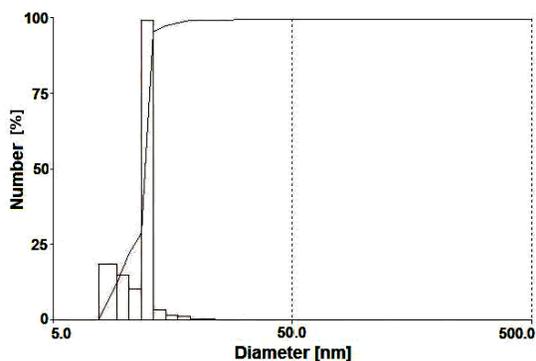

Fig. 5. The grain size distribution of SNPs in a solution having a concentration of 15 ppm.
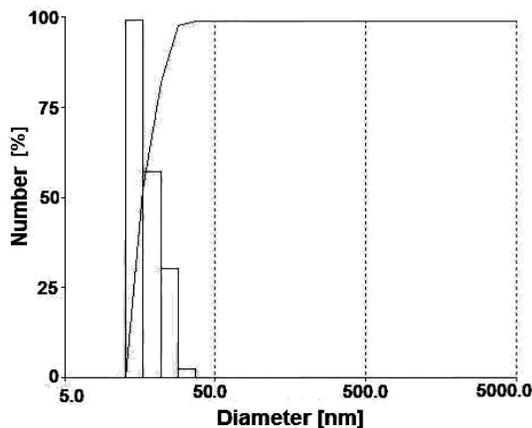

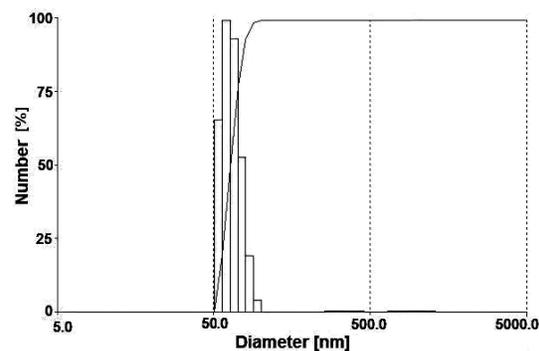*Fig. 6. The grain size distribution of SNPs in solutions having a concentration of 50 ppm.*

Fig. 7. The grain size distribution of SNPs in solutions having a concentration of 100 ppm.

The mean diameter of the CSS with a SNPs content of 15 ppm is of 16.5 nm, for the CSS with a SNPs content of 50 ppm is of 38.4 nm and for the CSS with a SNPs content of 100 ppm is of 69.2 nm. These data are in agreement with TEM analyses (Figs. 2-4).

It is important to know the size of the SNPs from the

CSSs, especially in medical applications which require nanoparticles having the mean diameter of about 10 nm. The size of the nanoparticles controls surface area, which in turn determines the CSS antibacterial efficiency, which in turn is influenced by quantity of released silver ions from SNPs. Achieving of some high defined SNPs (with controlled shape, closed grain size distribution, mean diameter as fine as possible, and high surface area) leads to products of high quality [3, 4]. Therefore, the best way to obtain a high antibacterial effect is the achieving of some SNPs as fine as possible in some stable solutions.

In Figs. 8-9 are presented the zeta potential curves (measurements of colloidal solution stability by the electrostatic repulsion between nanoparticles) of some CSSs with SNPs concentration of 15 ppm, 50 ppm and 100 ppm.
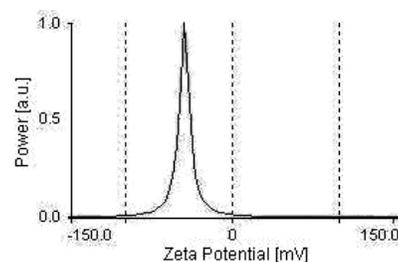

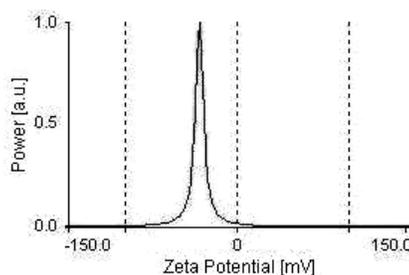*Fig. 6. The zeta potential of a CSS with a SNPs content of 15 ppm.*

Fig. 7. The zeta potential of a CSS with a SNPs content of 50 ppm.
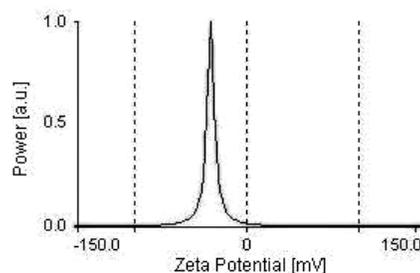

Fig. 8. The zeta potential of a CSS with a SNPs content of 100 ppm.

The zeta potential was – 44.82 mV for the CSS of 15 ppm concentration, - 33.55 mV for the CSS of 50 ppm concentration and – 31.88 mV for the CSS of 100 ppm

concentration. These results prove that the obtained CSSs are stable. We mention that the stable aqueous dispersions are characterized by a zeta potential smaller than -30 mV and higher than +30 mV, and the unstable aqueous dispersions are characterized by a zeta potential in the range of – 30...+30 mV [15].

The stabilization of SNPs solutions having concentrations up to 50 ppm was strongly enough to prevent the agglomeration of the colloidal particles and their deposition as metallic precipitates for six months. The high stability of CSSs is the result of the used procedure which controls the size and the dispersion of the particles by reducing of the surface energy through the stabilization with ionic and polymeric compounds (tri-sodium citrate and PVP, respectively). So, in the first step of synthesis, at temperatures ranging between 70-90° C, a part of citrate anions ($C_6H_5O_7{}^{3-}$) are oxidized simultaneous with reduction of Ag^+ ions to SNPs. The other part of citrate anions is adsorbed by the nucleophilic carboxylic groups on SNPs to form the first electrostatic protective layer. The second layer consisting of Na^+ ions is more diffuse and weak

The citrate ion adsorption induces a fractional electron transfer, which according with Henglein's work is summed over all the adsorbed molecules inducing a displacement of the metal Fermi level toward the more negative potentials.

In the same time, the carboxilyc group redox potential increases and become easier to photo oxidize [17]. The electronegative loaded SNPs in form of uni-and bi-dentate species are electrostatic stabilized. In this case, the citrate ions have both photo-reducing and electrostatic protective agent. The SNPs steric protection is realized by coordination with electron donating N atoms of the PVP pyrrolidyl ring. The TEM micrograph from Fig. 2 shows very clear these arrangements in which are observed SNPs covered by a layer of protective molecules.

Even the presented method seems to be easy at the first sight we had to be very carefully to obtain stable CSSs with reproducible characteristics. The purity of the water and of the reaction agents, as well as the cleanness of the laboratory vessels are critical parameters. The temperature of the solution, the concentration of the $AgNO_3$ and of the reduction agent and the reaction time duration influence the particles size.

Since we measured the CSSs monthly for a time period of six months, we noticed that the CSSs stability was kept, only a little displacement to the right of the UV-VIS absorbance peaks occurred due to a very little agglomeration tendency of the SNPs. The zeta potential of the CSSs remained almost the same.

4. Conclusions

The paper presents a method for obtaining by a chemical way some stable CSSs of variousconcentrations varying in the range of 5…100 ppm. These consist of monolayer-protected SNPs having a mean diameter up to 69.2 nm. The SNPs have mainly spherical shape but a minor fraction of elongated SNPs do appear at high concentration of CSS. Some narrow grain size distributions were obtained. The zeta potential of the studied CSSs varies in the range of – 44.82… - 31.88 mV. These values proved a high stability of the solutions.

The SNPs were homogenously dispersed in the solution due to the electrostatic repulsion between the electric double layers existent to each particle and due to the steric stabilization with PVP that prevented the electrical contacts among particles

The method elaborated by us for obtaining of some stable CSSs is very efficient, ecological, environmental friendly and can be up-scaled.

The obtained CSSs can be used successfully in different applications, depending on the SNPs concentration and size.

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