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Application of a voltammetric method for investigation the formation mechanisms of silver nanoparticles in multicomponent solutions

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Abstract A voltammetric method has been tested for the investigation of the kinetics of formation of silver nanoparticles in two systems: (a) silver(I) triflourineacetate, methylcellosolve, butyl acetate, toluene and methyl methacrylate with methacrylic acid copolymer; and (b) silver nitrate, sodium citrate, poly-N-vinyl-2-pirrolydone, sodium borohydride. It could be established for the first system that the formation rate of metal nanoparticles from silver triflourineacetate solutions depends on the dielectric constant and complexing ability of the solvent. The formation of silver particles proceeds faster in methylcellosolve than in other solvents. The butyl acetate addition to the solution contributes to the complex stability of methylcellosolve with silver triflourineacetate and decelerates the formation process of particles. It could be shown that nitrogen purging of solutions containing poly-N-vinyl-2-pirrolydone affects the silver-ion concentration in the first stage of synthesis and accelerates the formation process of nanoparticles for the second system. The spherical silver nanoparticles which are formed at the first stage of the synthesis are destroyed after starting the UV–irradiation. Then new silver nanoparticles (triangular prisms) are formed.

Introduction

There is a serious interest in the formation of silver nanoparticles because of the properties this material: large intensity of surface plasmon resonance band, high extinction coefficient, optical characteristics features of surface layer close to metal nanoparticles, giant Raman scattering phenomena and the bactericidal properties of colloidal silver solutions [1–16]. These systems should meet the following high requirements: product purity, narrow size distribution and time stability. It is necessary to explore carefully the formation mechanism of nanoparticles for the systems creating such properties. It is essential to note that the reduction mechanism of silver ions strongly depends not only on the solution composition [5, 10, 11, 15] but also on external factors: light, oxygen and carbon dioxide content, etc. [11, 17].

At the present time, there are a lot of methods available to control the size and shape of particles: raster electron microscopy, scanning probe microscopy, transmission electron microscopy, etc. [1, 18]. Optical spectroscopy of nanoparticles is more informative, and it is a routine method to study the kinetics of particle formation in solutions [1–4, 6, 7, 9, 10, 12]. This method allows obtaining reliable information on the reaction mechanism for particles smaller than 10 nm with a narrow size distribution because the absorption is proportional to the particles concentration [19, 20]. For a wide particle distribution, the application of optical

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spectroscopy is less convenient. For example, there is one band corresponding to the dipole resonance of small and big particles and a band corresponding to the quadrupole resonance of particles in an anisotropic particle spectrum. An optical spectrum description of solutions consisting of many components such as stabilizers, reducers and some solvents makes the analysis of the reaction mechanism even more complicated, and other methods have to be applied in addition [21, 22].

In our work we propose using voltammetry [23, 24] to study the formation process of silver nanoparticles. The control of the changes in silver-ion concentration in the solution is useful for getting additional information about the kinetics of the particles formation as the silver-ion content decreases during the synthesis process. Two research objects have been chosen. The first system contained silver triflourineacetate (CF_3COOAg), methylcellosolve (MC), butyl acetate (BA), toluene (Tol) and methyl methacrylate (MMA) with methacrylic acid (MAA) copolymer system [21]. The second system contained silver nitrate ($AgNO_3$), sodium citrate (Na_3Cit), poly-N-vinyl-2-pirrolydone (PVP) and sodium borohydride ($NaBH_4$) [10, 25]. The first system allows the synthesis of spherical particles in a non-aqueous medium, whereas the second system, an aqueous, allows the synthesis of triangular prisms.

Materials and procedures

Techniques to study the formation of silver nanoparticles in the system CF_3COOAg, MC, BA and Tol

CF_3COOAg solutions (0.005 M) in individual solvents and their mixtures were prepared for the experimental studies: methylcellosolve to butyl acetate (90:10 vol%), methylcellosolve to toluene (90:10 vol%), methylcellosolve to butyl acetate to toluene (75:15:10 vol%) and methylcellosolve to butyl acetate to toluene to MMA with methacrylic acid (MAA) copolymer. The first derivative of cyclic voltammograms of CF_3COOAg solutions was recorded by means of a polarograph (PU-1) in a three-electrode cell with a scan rate of 30 mV/s. A paraffin-impregnated graphite (GE) was used as an indicator electrode. The investigated solvents containing 0.2 M CF_3COOK were used as background electrolytes. The electrode surface was polished with a filter paper and placed into dithizone CCl_4 solution after every recording of a voltammetric curve. The investigated solvents mixtures containing CF_3COOAg were added to the background electrolyte in a suitable ratio 1:19 (volume percent). The spectrophotometer Specord M-40 was used to record the absorption spectra of the solvents, and the Ag(I) solutions in quartz cuvettes (1-cm path length) in the wavelength range from 260 to 900 nm.

The phase composition of the prepared particles was analysed using the voltammetric method with a carbon–paste electroactive electrode [24]. Following the separation of the silver samples from the synthesis solution, they were mixed with graphitic powder and an organic binder (paraffin with melting point 70 °C) in the ratio 1:10:10 (mass percent), respectively. This mixture was heated as to allow melting of the paraffin, carefully mixed and placed in a fluoroplast tube. The fabricated electrode was inserted into an electrochemical cell, and the first derivatives of cyclic voltammograms were recorded with a scan rate of 30 mV/s. The background electrolyte was 0.02 M $NaClO_4$ in ethylene glycol.

Techniques to study the formation of silver nanoparticles in the system $AgNO_3$, Na_3Cit, PVP and $NaBH_4$

The silver nanoparticles were prepared by a photochemical reduction method. The reaction was performed in an aqueous solution of $AgNO_3$ (1×10^{-4} mol/l), PVP (4.5×10^{-3} mol/l), Na_3Cit (4.2×10^{-4} mol/l) and $NaBH_4$ (5×10^{-3} mol/l). The mixture of solutions containing $AgNO_3$, PVP and Na_3Cit was purged with nitrogen through a glass filter (pore diameter is 3 μm) during 20 min after mixing. The prepared mixture was placed on a magnetic stirrer, and the $NaBH_4$ solution was added within 15 min. The synthesis was then continued by UV–irradiation during a few days until a constant blue colour appeared [25].

The formation of silver nanoparticles was studied by voltammetry as follows: A glassy carbon (GC) electrode was placed for 15 min in the reaction system containing the formed silver nanoparticles. After that the electrode was placed in the electrolytic cell and the voltammetric curve was recorded which revealed the presence of adsorbed silver particles. In the first stage of the synthesis, the sampling was made every 30 min (during 5 h), after that it was made every 12 h. The polarograph PU-1 for the VA analysis was used. The first derivative of cyclic voltammograms was recorded in the three-electrode cell in the potential range −1.0 to +1.0 V using a scan rate of 20 mV/s. The background electrolyte was 0.05 M Na_3Cit. Auxiliary and reference electrodes were silver wires placed in glass tubes filled with the background electrolyte.

Scanning electron microscope was used to image the prepared particles and to image their adsorption on the GC electrode surface used for the voltammetric measurements. The GC wafers were dipped into the solution with the silver nanoparticles for 15 min. Thereafter images of the GC surface pictures were recorded by means of the scanning electron microscope SEM 515 with a gun power of 15.2 kV. Transmission electron microscopic pictures were obtained with a JEM−100CXII using a beam energy of 80 keV.
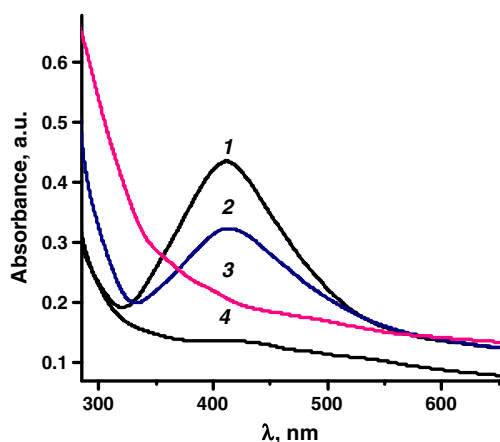
Fig. 1 Time-dependent evolution of UV–vis absorption spectra for CF$_3$COOAg solution in MC (*1*, *4*) and MC–BA–Tol system (*2*, *3*) registered 15 min (*1*, *2*) and 24 h after the solution preparation (*3*, *4*)

Results and discussions

The study of Ag nanoparticles formation in the system CF$_3$COOAg, MC, BA and Tol

In this part of work, the formation of silver nanoparticles was studied in different organic media, i.e. in methylcellosolve, butyl acetate, toluene and their mixture as well as methyl methacrylate–methacrylic acid copolymer with the solvents mixture solution. Probably, methylcellosolve is a main reducing agent in the solution since the properties of glycols are well-known [26]. Since the reaction proceeds under visible light and it is possible that this also affects the reaction. In these systems the synthesis of nanoparticles passes through a series of complexes stage. The rate of particle formation and the role of every component in this process can be determined by identifying some compounds and estimating their relative stability in the solution. The processes proceeding in the CF$_3$COOAg organic solvent system were studied by recording the absorption spectra of these systems and by voltammetry.

According to ASM data, the particles (particle size is 50–500 nm) are formed in the solvents mixture within 1 h after salt dissolution [21]. The absorption band with a maximum at 415±10 nm (Fig. 1) corresponds to the silver nanoparticles. This absorption band is due to fluctuations of free electrons in the surface layer of the nanoparticles [10]. The decrease of the absorption intensity for CF$_3$COOAg, MC, BA and Tol is observed (curves 2, Fig. 1) in comparison with the absorption intensity of CF$_3$COOAg and MC (curves 1, Fig. 1). It indicates the influence of butyl acetate and toluene on the formation process of metal particles.
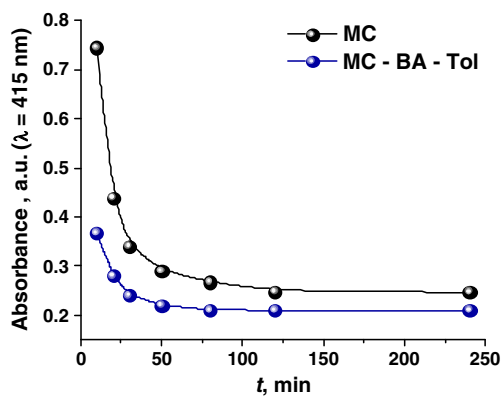
The existence of silver(I) complexes with different organic ligands was shown by means of the voltammetry. Figure 2 shows the first derivative of cyclic voltammograms

recorded in CF$_3$COOAg solutions. The reduction potentials of the silver complexes show that their stabilities vary in the different media. More negative potential was observed for methylcellosolve, butyl acetate and toluene mixture (Fig. 2, curve 4). It is evident that the nanoparticles formation rate for this system should be the slowest because a stronger compound from Ag$^+$ with CF$_3$COO$^-$ and solvent molecules is formed. The reduction of the silver ions is observed at more positive potentials in methylcellosolve (Fig. 2, curve 1). Therefore, a relatively high rate of particle formation is expected in that solvent. In spite of methylcellosolve being the main solvating ligand in all mixtures possessing enough reactivity, significant differences in the cathodic parts of the voltammograms show that butyl acetate also takes part in the coordination of silver ions: their reduction potential in methylcellosolve and butyl acetate system is displaced to more negative values (Fig. 2, curve 2). The reduction potential is not changed by addition of toluene to methylcellosolve (Fig. 2, curve 3).

Figure 3 shows time dependencies of the absorption of solutions at λ=415 nm. The absorption decrease is followed by a colour change of the solution that, probably, is caused by a decrease of concentration of nanoparticles in the solution caused by their aggregation and deposition as solid phase. A black deposit (particle size is >1 μm) is observed in the solution after 24 h. The absorption band in the range 330 to 550 nm disappears in the electronic spectra of the solutions. The observed absorption differences for CF$_3$COOAg solutions in methylcellosolve and solvents mixture, probably, are connected with a deceleration of
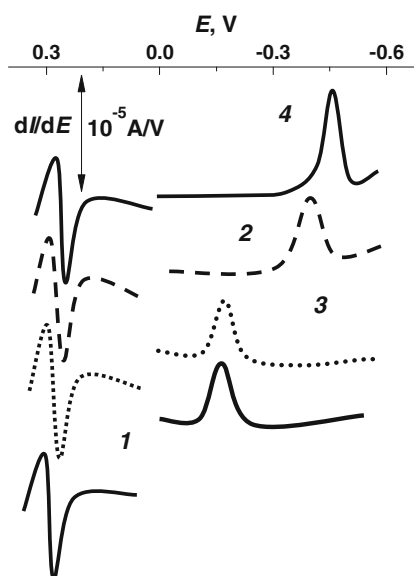
Fig. 2 Fragments of the first derivatives of cyclic voltammograms of CF$_3$COOAg in MC (*4*), in MC and Tol (*3*), in MC and BA (*2*) and in MC, BA and Tol solutions (*1*)
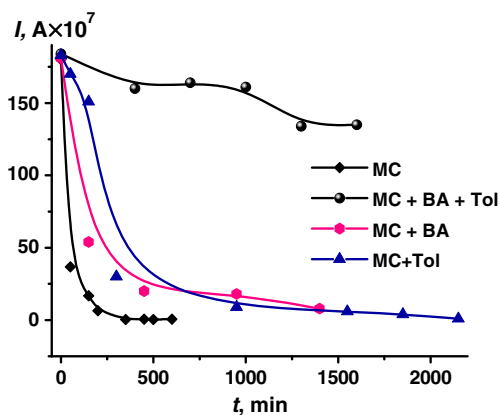
Fig. 3 Absorption change ($\lambda=415$ nm) for CF$_3$COOAg, organic solvents system on time

Fig. 5 Time-dependent evolution of UV–vis absorption spectra for the system CF$_3$COOAg, MMA, MAA, MC, BA and Tol
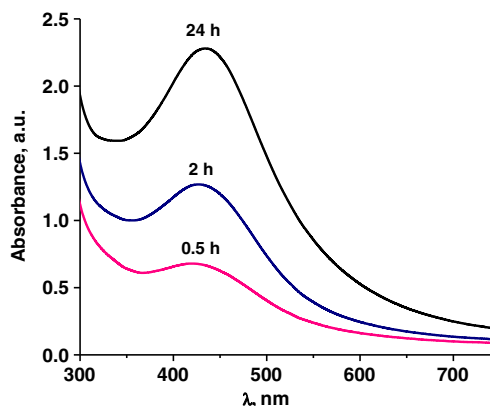
particle formation and deposition in methylcellosolve–butyl acetate–toluene system.

To confirm this hypothesis, the dependence of silver-ion concentration on time was studied in the mentioned solvents with the voltammetric method. The reduction current of silver ions was chosen as analytical signal. The dependencies of the reduction current (proportional to silver ions content) on time show that this assumption is correct (Fig. 4). The ion content decreases much faster in methylcellosolve compared to other solvents. The deposition process of silver particles is the slowest in the methylcellosolve, butyl acetate and toluene system: a significant decrease of the silver-ion concentration is observed only after 15–20 days.

According to optical spectroscopy, the reduction of silver-ion reduction is accompanied in MMA and MAA copolymer solution in organic solvents by a shift of the absorption maximum to longer wavelengths ($\lambda_{max}=430\pm10$ nm; Fig. 5). This shift of the absorption band and its asymmetry can be caused by the interaction of copolymer
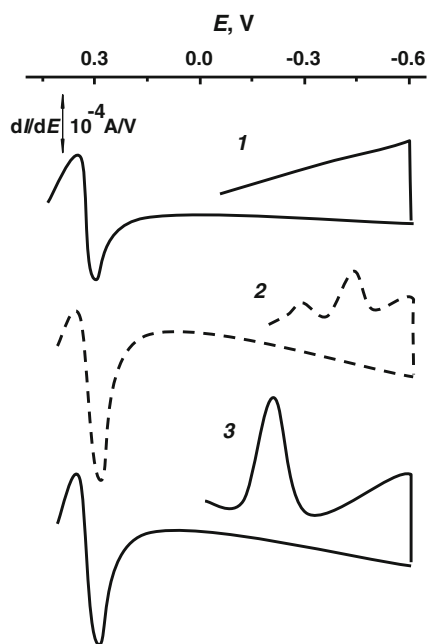
molecules with the formed nanoparticles resulting in an electronic state change on a particle surface. The copolymer molecules prevent further growth of the particles.

On the basis of the given results, the copolymer molecules take part in the formation of silver nanoparticles. In particular, they promote a simultaneous nucleation and they stabilize the nanoparticles, inhibiting their growth.

The formation of large dispersed silver particles is faster in methylcellosolve than in other solvents. The addition of butyl acetate to the solution promotes the complex stability of methylcellosolve with the CF$_3$COOAg complex and decelerates the formation of nanoparticles. Probably, the toluene influence is connected with its low dielectric constant which decelerates the silver particles formation. The reduction of the silver ions is accompanied in organic solvents by a fast particle growth and subsequent particle deposition. The copolymer molecules react with the nanoparticles and prevent their aggregation, leading to stable suspensions.

A carbon–paste electrode was used to study the silver nanoparticles formed in the polymer solution. To prevent alterations of the surface composition, a non-aqueous solvent (ethylene glycol) was used.

The silver particles were formed in the polymer solution–CF$_3$COOAg system, and voltammetry was used for the identification of the phase composition of the precipitated and separated particles (Fig. 6, curve 1), and for particles covered by the polymer after the separation of the solvent (curve 2). For comparison the electrochemical behaviour of CF$_3$COOAg was studied (curve 3). The absence of a reduction signal in the polymer–nanoparticles system corroborates that almost all silver is in the element state. Two signals were observed in the reduction curve of already precipitated particles. This means that the silver is partly in an oxidized state. Since the oxidation signal is obviously larger, it seems that most of the silver is in elemental form.

Fig. 4 The reduction current of silver ions as function of reaction time for different solvents (the reduction current is proportional to the silver concentration)

Fig. 6 Cyclic voltammograms of CPEE containing silver nanoparticles covered by the polymer (*1*), precipitated particles (*2*) and silver triflourine acetate (*3*)

The study of the formation of silver nanoparticles an aqueous solution of poly-*N*-vinyl-2-pirrolydone

It was one of the objectives of this study to elucidate the role of each of the chemical components (AgNO₃, Na₃Cit, PVP and NaBH₄), and that of the nitrogen purging and irradiation on the formation of the silver nanoparticles. Therefore, the system was studied in such way that each of these components was excluded in one of the experiments. In this case, it is very hard to use the same technique which was applied for the first system study (a solution sampling) as the solution resistance strongly increased during the synthesis (up to 2 MΩ cm). The sampling was performed as follows: the
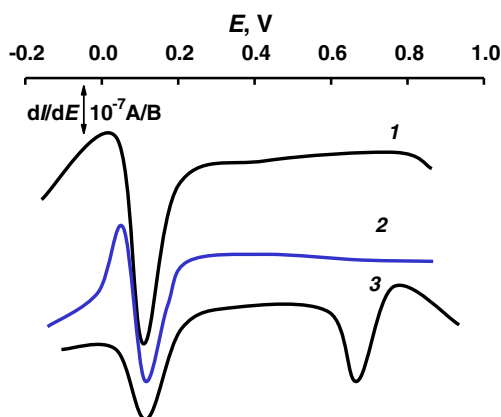
**Fig. 7** Anodic voltammograms of a GC electrode after adsorption process in AgNO₃, Na₃Cit (*1*); AgNO₃, Na₃Cit, PVP, NaBH₄ (*2*); AgNO₃, Na₃Cit, PVP, NaBH₄ after the irradiation during 24 h (*3*)

GC electrode was placed in the system with the silver nanoparticles for 15 min. When the GC electrode was introduced to the silver particle solution, silver ions and small clusters may be reduced on the GC electrode, and the current signal will be proportional to the silver-ion concentration. At the same time, large colloidal particles and nanoparticles can be absorbed on the GC surface and can give a respective electrochemical response. Figure 7 shows the anodic voltammetric curves for the GC electrode recorded after its removal from the aqueous solutions containing AgNO₃–Na₃Cit (curve 1) and all the components (curves 2 and 3). Obviously, the signal at 0.1 V observed in all systems is caused by the elemental silver. The voltammetric curves of the system containing all components show a signal at 0.7 V. Apparently, it corresponds to the silver existing in the solutions in larger aggregates, the largest of them are displayed in X-ray microscopy pictures of the GC surface (Fig. 8). This signal does not always appear because most of the large aggregates either cannot be adsorbed on the electrode or they are electrochemically inert: it is assumed that this signal corresponds to colloidal particles covered by PVP macromolecules. Thus, the signal at 0.1 V is more suitable for studies of the kinetics of the silver nanoparticle formation. At this potential, the dependence of current on silver-ion concentration in AgNO₃–Na₃Cit solutions is linear in the range at $5 \cdot 10^{-4}$ to $5 \cdot 10^{-7}$ mol/l. Figure 9 shows the effect of nitrogen purging on the loss of silver ions during the formation of nanoparticles. The nitrogen purging accelerates the particles formation in the first synthesis stage. The obtained silver particles are almost identical in both cases
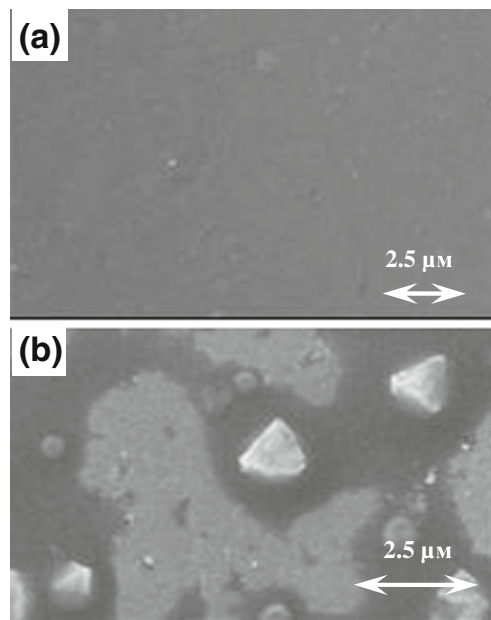
Fig. 8 X-ray microscopy pictures of the GC surface before (**a**) and after extract from AgNO₃, Na₃Cit, PVP and NaBH₄ solution irradiated during 48 h (**b**)
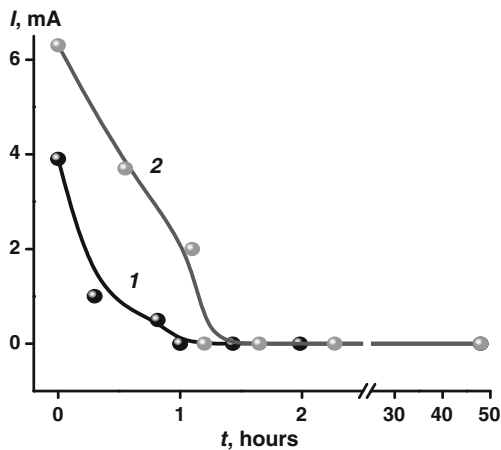
Fig. 9 The irradiation time influence on the oxidation current showing silver ions content in AgNO₃, Na₃Cit, PVP, NaBH₄ solution: with the purging (*1*) and without the purging (*2*)

(Fig. 10), the main difference is their formation rate. One of the most probable explanations of the nitrogen purging effect is that oxygen being an oxidant is removed from the solution. However, Fig. 11a shows the increasing of the ions concentration in solution during the purging process (every second point on the diagram).

This effect is stronger for solutions containing PVP (curves 1–3; Fig. 11a). Thereby the silver ions are released during the

purging process. We can suppose that the polymer absorbs on the gas molecules, changes the chain conformation and, as consequence, the particles connecting with the copolymers are destroyed.

Generally, in the last phase of synthesis, anisotropic triangular shaped particles are formed, whereas large spherical particles exist in the in the first stage of synthesis. The mechanism of formation of silver nanoprisms has been described in [5]. There it has been proposed that the triangular nanoparticles are formed not directly from silver ions but by a conversion process from the large spherical particles. This process happens under UV irradiation due to a destruction of the spherical particles formed in the first stage. It is very difficult study the influence of irradiation on the process (Fig. 11a). The additional amount of the silver ions appears both during UV irradiation and purging. To estimate the effect of irradiation on the silver nanoparticle formation, a voltammetric analysis of the system was made without nitrogen purging (Fig. 11b). After starting the irradiation, a maximum appears (every fourth point) on dependencies registered for the systems containing PVP (curves 1–3; Fig. 11b). These results show that the spherical silver nanoparticles which formed at the first step of the synthesis are destroyed after starting the UV irradiation. Afterwards, the new silver nanoparticles (triangular prisms) are

Fig. 10 TEM pictures of silver particles synthesized without the purging (**a**, **c**) and with the purging (**b**, **d**)
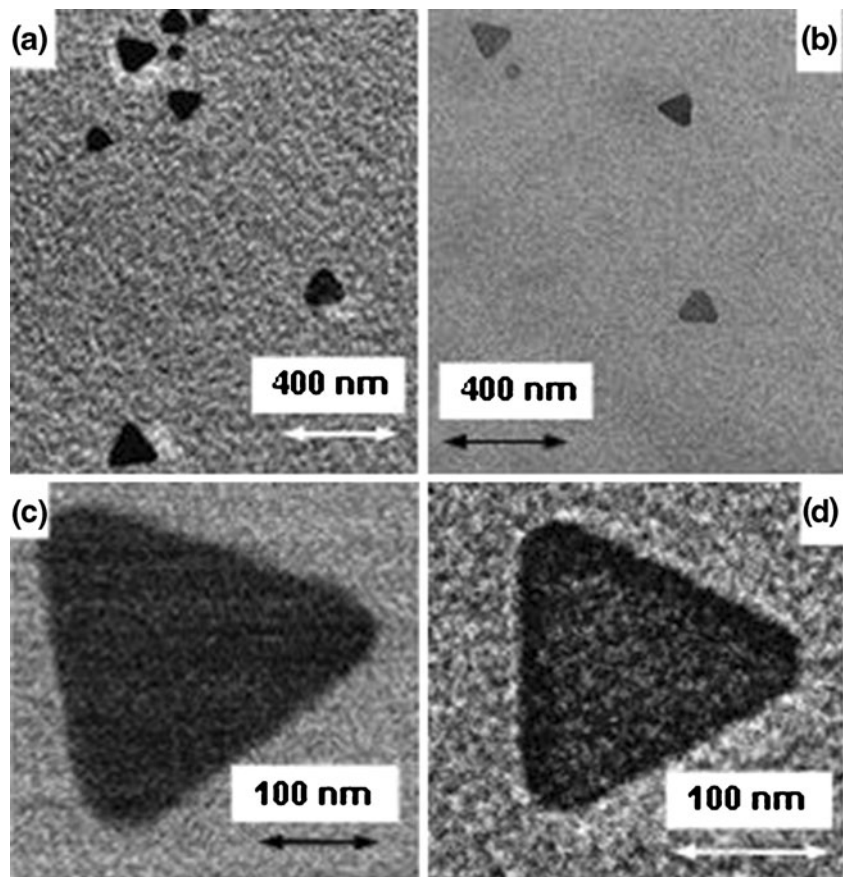
Fig. 11 The synthesis time influence in different water solutions with the purging (**a**) and without the purging (**b**) on the oxidation current demonstrating silver ions content for $AgNO_3$, PVP, $NaBH_4$ (*1*); $AgNO_3$, PVP (*2*); $AgNO_3$, Na_3Cit, PVP (*3*); $AgNO_3$, $NaBH_4$ (*4*); $AgNO_3$, Na_3Cit, $NaBH_4$ (*5*)
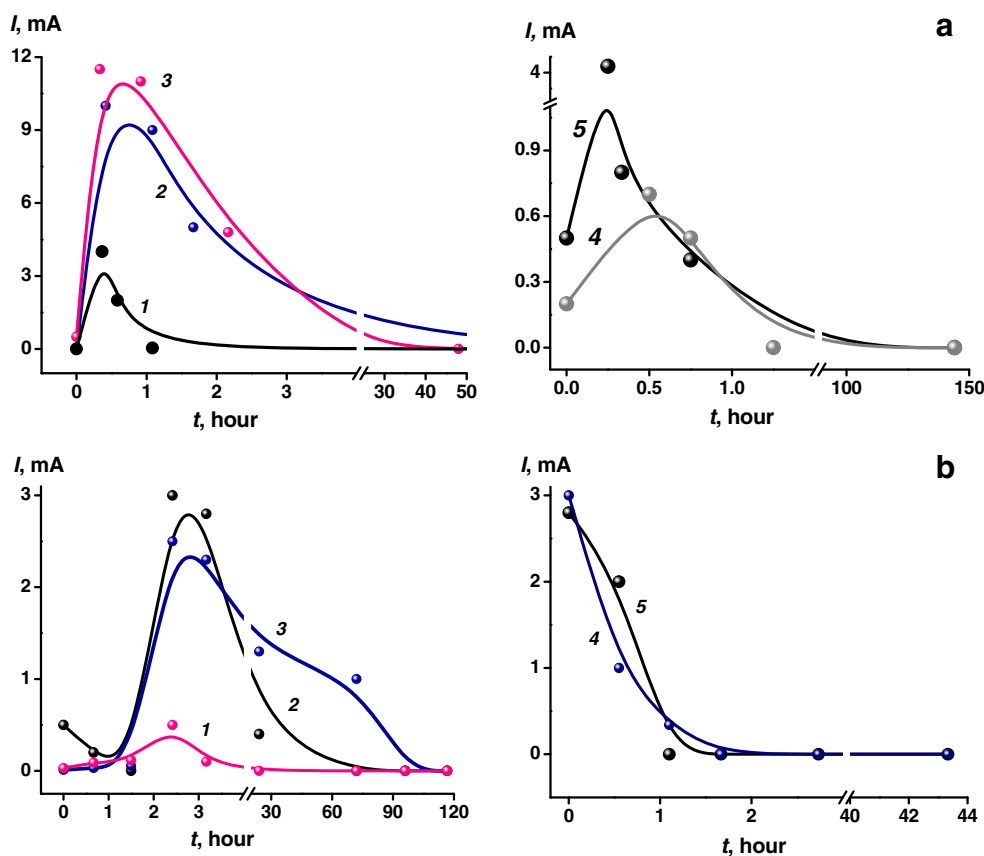
formed. Mainly, the destruction of the particles adsorbed on PVP that happens because of the UV irradiation of the solution without PVP does not lead to increasing of the silver ions.

On the basis of the given results, we can identify the role of citrate anions in the synthesis of silver nanoparticle. It is evident (curves 1, Fig. 11a, b) that the formation of large aggregates is getting faster in the presence of citrate, and triangular nanoprisms are not formed in the last stage of synthesis, as could be seen from TEM images. This is certainly caused by a stabilization of the particles formed at the beginning of synthesis by polymer molecules and also citrate ions. The destruction of citrate happens on the surface of the silver particles during irradiation [5, 14].

From the given features (Fig. 11), it is possible to conclude that the particle formation happens in the solutions containing any system components; as in all cases, a decrease of the silver ions content is observed. However, the triangular particles are formed only in the presence of all components in the solution according to TEM data. A precipitation of particles does not occur in this system.

The solution colour containing all components changes during the synthesis process from transparent, to yellow, to green and finally to blue (Fig. 12). It is essential to note that compared with the voltammetric and spectroscopic data of the system, the effects occurring during the nitrogen purging stage are not observable in spectroscopy. On the contrary,

the UV spectroscopy is a more sensible method to follow the early stages of synthesis.

On the basis of the given results obtained by voltammetry, PEM, REM and optical spectroscopy, described in detail in [21, 25], it is possible to suggest the following mechanism of formation of silver nanoparticles: Colloidal silver particles are formed initially during the mixing of the reagents in the solution. They can be stabilized either by citrate ions or by
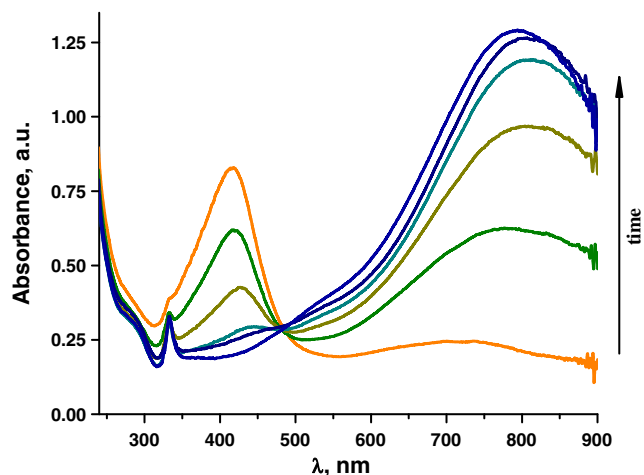
Fig. 12 Time-dependent evolution of UV–vis absorption spectra for $AgNO_3$, PVP, $NaBH_4$ and Na_3Cit

macromolecules *and* citrate ions. The nitrogen purging prevents the formation of larger aggregates from these particles. Some silver ions are released during this process. The other silver ions are reduced by the irradiation. The already formed particles are destructed before the irradiation. Citrate ions are also decomposed on the surface of the particles during irradiation. Either charged clusters or small-sized particles are formed during the particles destruction. These particles are the source of silver ions for the formation of anisotropic particles. The particle destruction products are bound to the polymer chains. Then, conformational changes of the polymer chain happen when the aggregates are formed. The coalescence of the aggregates occurs together with the decomposition of in the last phase of synthesis.

Conclusions

A voltammetric method has been tested for the investigation of the formation of silver nanoparticles in organic and aqueous solutions. It was established that the formation rate of metal nanoparticles from silver triflourineacetate dissolved in the methylcellosolve, butyl acetate and toluene mixture depends on the dielectric constant and complexing ability of the solvent. It was shown that the formation of silver particles proceeds faster in methylcellosolve than in other solvents. The addition of butyl acetate to the solution contributes to stability of the complex of methylcellosolve with silver triflourineacetate and decelerates the formation process of the nanoparticles.

It was shown that the nitrogen purging of solutions containing poly-*N*-vinyl-2-pirrolydone leads to the enrichment of solution of the silver-ion concentration at the first stage of synthesis and speeds up the formation process of the nanoparticles. It is established that the spherical silver nanoparticles which formed at the first stage of the synthesis are destroyed after starting the UV irradiation. Then new silver nanoparticles (triangular prisms) are formed. Therefore the UV irradiation and the nitrogen purging have an identical effect on the process of formation of silver nanoparticles such as destroying of the spherical nanoparticles and growing of triangular prisms.

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