

METHYLVIologen MEDIATED ELECTROSYNTHESIS OF SILVER NANOPARTICLES IN A WATER MEDIUM. EFFECT OF CHAIN LENGTH AND CONCENTRATION OF POLY(N-VINYLPYRROLIDONE) ON PARTICLE SIZE

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Abstract. Efficient electrosynthesis of spherical silver nanoparticles (AgNP) stabilized by poly(*N*-vinylpyrrolidone) (PVP₄₀ and PVP₁₃₀₀) in the solution bulk in single compartment cell has been performed using a soluble silver anode as *in situ* supplier of Ag⁺ ions in water/ 0.1 M KNO₃ medium. AgNP are obtained as a result of the methylviologen mediated electroreduction of Ag⁺ ions at the potentials of the MV²⁺/MV⁺ redox couple and the dispersion of the Ag-anode. The total current yield of AgNP (106 ÷ 163%) increases and the particle size decreases with increasing the PVP concentration. In the presence of PVP₁₃₀₀, the particle size is noticeably higher than in the presence of PVP₄₀. The possibility of controlling the AgNP size in a sufficiently wide range from 26 ± 6 to 61 ± 12 nm is shown by varying the nature and concentration of PVP.

Keywords: *electrosynthesis, nanoparticle, silver, mediator, methylviologen, polyvinylpyrrolidone.*

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1. Introduction

In the last few decades, metal nanoparticles (MNP) are among the most actively studied nanoobjects. Of particular interest is their unique physical and chemical properties and a wide variety of potential applications in catalysis, biomedicine, optics, electronics, sensors, etc. (Daniel & Astruc, 2004; Dykman, 2008; Kharisov *et al.*, 2012; Pomogaylo, 2002; Roldughin, 2000; Suzdalev, 2009; Volkov *et al.*, 2013). MNP are obtained using physical, chemical, biochemical and electrochemical methods. At the beginning of the active phase of the MNP development, physical methods based on evaporation of solid metal under various physical effects and subsequent condensation of atoms to form NP were considered more promising. At present, chemical reduction of metal ions in solution using different reducing agents is the most successful and popular method for their synthesis. Biochemical methods have found limited application in the MNP preparation, there are only some examples of the synthesis of gold, silver, copper, and zinc NP (Egorova, 2004, 2010). The electrochemical method is widely used to obtain MNP immobilized on a conducting substrate (electrode) (Petrii, 2015) and is rather rarely used for MNP preparation in solution bulk. This is mainly due to the fact

that metals generated during the reduction of their ions are deposited on an electrode. Therefore, in electrosynthesis of MNP in solution, the problem of metal deposition has to be solved or another way of MNP preparation without reduction of metal ions is used. Several such methods are known: the dispersion of a massive metal electrode during electrolysis (Haber, 1898; Leontyev *et al.*, 2012), the electroreduction of metal ions by the method of pulsed sono-electrochemistry (Reisse *et al.*, 1996; Saez and Mason, 2009; Zhu *et al.*, 2000) or in the presence of salts of surface-active cations R_4N^+ or R_4P^+ (Becker *et al.*, 1995; Li *et al.*, 2015; Mohamed *et al.*, 1999; Reetz and Helbig, 1994; Reetz *et al.*, 1995a, 1995b, 1996, 2001; Vilar-Vidal *et al.*, 2010; Yu *et al.*, 1997).

The method of mediated electrosynthesis of MNP devised by us has proved effective in the preparation of MNP (Fig. 1) (Fedorenko *et al.*, 2015; Kokorekin *et al.*, 2017; Nasretdinova *et al.*, 2015a, 2015b, 2016, 2017, 2018; Yanilkin *et al.*, 2014a, 2014b, 2015a, 2015b, 2015c, 2016a, 2016b, 2016c, 2016d, 2017a, 2017b, 2017c, 2017d, 2017e, 2017f, 2017g, 2017h).

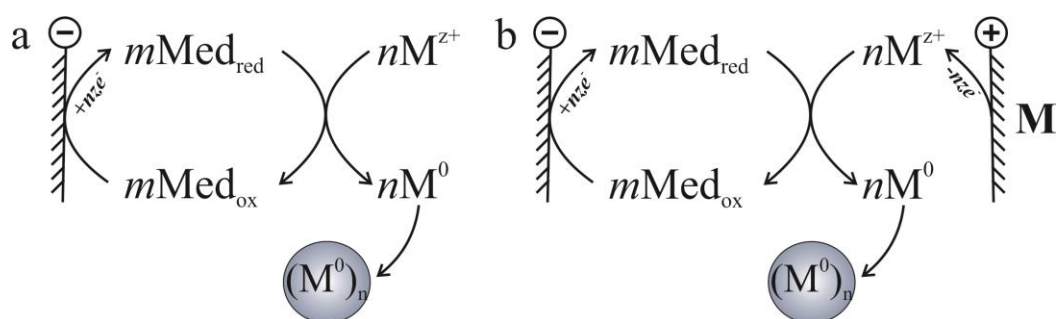
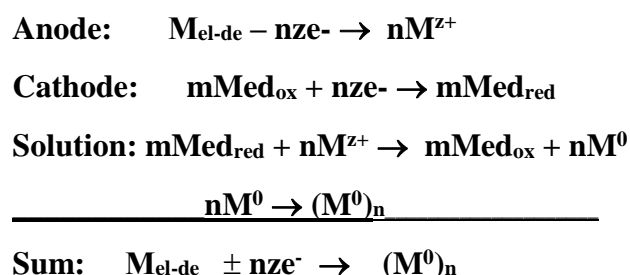


Figure 1. Scheme of the mediated electrosynthesis of MNP $(M^0)_n$ in solution bulk (a) in diaphragm cell and (b) in single compartment cell using a soluble anode.

A feature of the method is that the process of metal ion reduction moves from the electrode surface to the solution bulk. A mediator is reduced on the electrode, then reduced form of the mediator diffuses into the solution bulk and reduces metal ion there. Thus, metal deposition on the electrode is minimized or completely avoided and MNP are obtained in the solution bulk. Under the conditions of electrolysis in a diaphragm cell (Fig. 1a), metal ions are usually added to the solution as a corresponding salt or complex (Fedorenko *et al.*, 2015; Nasretdinova *et al.*, 2015a, 2015b, 2016, 2017, 2018; Yanilkin *et al.*, 2014a, 2014b, 2015a, 2015b, 2015c, 2016b, 2016c, 2016d, 2017b, 2017c, 2017d, 2017e, 2017f, 2017h), and in the case of electrolysis in a single compartment cell, metal ions are generated *in situ* using a soluble anode (Fig. 1b) (Kokorekin *et al.*, 2017; Yanilkin *et al.*, 2016a, 2017a, 2017g). The electrolysis in a single compartment cell is more attractive because it is simple for experimentation and scaling. Unlike all chemical, biochemical and other electrochemical methods of MNP preparation, theoretically, the only result of the proposed technique is the conversion of a massive metal into MNP (Scheme 1) in solution. This corresponds to the principles of "green chemistry".

This variant of the mediated electrosynthesis was used to produce gold (Yanilkin *et al.*, 2017g), copper (Kokorekin *et al.*, 2017), and silver (Yanilkin *et al.*, 2016a, 2017a) NP. In the latter case, the process is particularly effective: the dispersion of the anode occurs along with dissolution, and so the total current yield of MNP is higher than 100%.



Scheme 1. Mediated electrosynthesis of MNP $(\text{M}^0)_n$ in the solution bulk using a soluble anode.

Properties of MNP depend on the size and shape of the particles. Therefore, recently emphasis is being placed on the development of methods for the synthesis of monodisperse particles of a certain size and shape. Among the many factors determining these characteristics of particles, one of the important is the nature of MNP stabilizer and the metal/stabilizer ratio. Poly(N-vinylpyrrolidone) (PVP) is widely used as a stabilizer of MNP, and using it we have performed a number of mediated electrosynthesis of MNP (Kokorekin *et al.*, 2017; Nasretdinova *et al.*, 2015a, 2015b; Yanilkin *et al.*, 2016a, 2016b, 2017a, 2017c, 2017e, 2017g). In connection with the above, in this report, the effect of chain length and concentration of PVP on the size of AgNP obtained in methylviologen mediated electrosynthesis in a single compartment cell in an aqueous medium was investigated.

2. Experimental part

Reagents. Commercially available KNO_3 , $\text{MV}^{2+} \cdot 2\text{NO}_3^-$ («Acros Organics») salts, poly(N-vinylpyrrolidone) PVP (40 000 and 1300000 D) («Alfa Aesar») were used without additional purification. All salts dissociate fairly well in used media, therefore we operate mainly with ions.

The study was performed using cyclic voltammetry (CV), microelectrolysis, preparative electrolysis, scanning (SEM) and high resolution transmission electron microscopy (TEM), UV-visible spectroscopy (UV-VIS).

CV. Cyclic voltammograms (CV curves) were recorded using a P-30S potentiostat (without IR compensation) (Elins, Russia) in an argon atmosphere. A glassy carbon (GC) disc electrode (dia. 3.4 and 2.0 mm) embedded in Teflon and sealed into a glass tube was used as the working electrode. Prior to each measurement, the electrode was mechanically polished. A platinum wire was used as the auxiliary electrode. Potentials were measured and reported *versus* an aqueous saturated calomel electrode (SCE) connected to the solution being studied through a bridge containing the supporting electrolyte and having a potential of -0.41 V relative to formal potential E_0' $\text{Fc}^{+/0}$ (internal standard). The temperature was 295 K.

Preparative electrolysis. It was carried out in a three-electrode single compartment glass cell in potentiostatic mode in an argon atmosphere at room temperature ($T = 295$ K) using a P-30S potentiostat. The solution was stirred with a magnetic stirrer during the electrolysis. A GC plate ($S = 3.7$ cm²) was used as the working electrode; a silver wire ($S = 1.7$ cm²) was used as the auxiliary electrode; an

SCE was used as the reference electrode. The latter was connected with the solution being studied through a bridge containing the supporting electrolyte. After completion of the electrolysis, the resulting solution was studied by CV using the indicator GC electrode (dia. 3.4 and 2.0 mm) directly in the cell.

A working solution (20 ml) for the electrolysis was prepared by dissolving 12.4 mg $MV^{2+} \cdot 2NO_3^-$ (2 mM), 202 mg KNO_3 (0.1 M) and different amounts of PVP: 0.6 mg (0.03 g/l), 3.3 mg (0.16 g/l), 10 mg (0.50 g/l), 20 mg (1.00 g/l), 36.6 mg (1.80 g/l) and 166.5 mg (8.30 g/l), which corresponds to a concentration of monomer units of 0.3, 1.5, 4.5, 9.0, 16.5 and 75 mM, respectively.

For the study by SEM, HR TEM and UV-VIS AgNP obtained in the electrolysis were precipitated by centrifugation (14 500 rpm, 1 hour), were washed twice with water and twice with ethanol, and were dispersed in ethanol by sonication. The washing consisted in the dispersing in a solvent by sonication and subsequent precipitation by centrifugation (14 500 rpm, 30 min). The resulting precipitate was dispersed in ethanol by sonication. For SEM, the resulting solution was applied onto a titanium foil surface preliminarily cleaned by ultrasonic treatment in water and in acetone. After that, the sample was dried at room temperature. In the case of HR TEM, 10 μ l of the solution was placed on a 3 mm copper mesh with formvar/carbon (Formvar/Carbon, Lacey Formvar) support and dried at room temperature. After complete drying, the mesh in a special graphite holder was placed into a transmission electron microscope in order to perform the microanalysis.

Electron microscopic analysis. The SEM studies were carried out using a Merlin field emission scanning electron microscope (Carl Zeiss, Germany). The surface morphology was imaged in the secondary electron (SE) mode with the primary electron accelerating voltage of 5 kV and with a probe current of 300 pA, to minimize the exposure to the object of study. To detect phase contrast, the accelerating voltage of primary electrons was 20 kV, and the probe current was 1 nA. The survey was carried out in the back-scattered electrons (AsB) mode. The microscope was equipped with an AZtec X-MAX energy dispersion spectrometer (Oxford Instruments, Great Britain) with resolution of 127 eV. The precision of measurement was 0.01-1%. The elemental analysis was carried out at an accelerating voltage of 20 keV and a flange focal length of 9.6 mm, which allowed minimizing the errors. The probing depth was less than 1 μ m. In the quantitative analysis, a set of etalons incorporated to the Aztec program (reference standart for X-RAY microanalysis "Registered Standart No. 8842") was used.

TEM-studies were carried out in the HR-TEM mode using a Hitachi HT 7700 Excellence transmission electron microscope (Japan) at an accelerating voltage of 100 keV with resolution of 0.144 nm. The elemental analysis was carried out using an Oxford Instruments X-Maxⁿ 80T attachment (Great Britain) equipped with a special holder.

UV-VIS. Absorption spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer (USA).

3. Results and discussion

There are peak of Ag^+ ions reduction ($E_{Cl} = 0.08$ V vs. SCE) and peak of deposited metallic silver reoxidation ($E_{Al} = 0.45$ V) on the CV curves of Ag^+ ions

recorded on the GC electrode in water/ 0.1 M KNO₃ medium in the absence and in the presence of PVP (Fig. 2, Yanilkin *et al.*, 2016a).

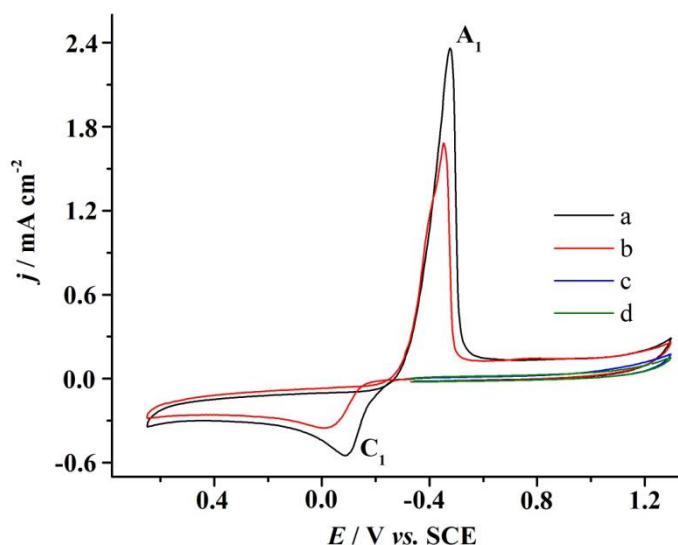
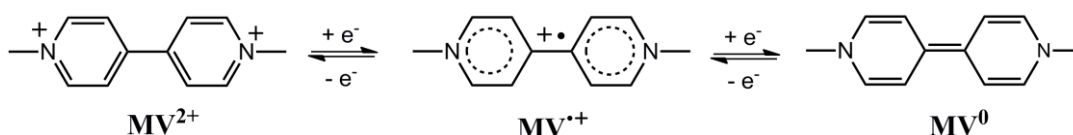


Figure 2. CV curves of Ag⁺ (1.5 mM) in the absence (a,c) and in the presence (b,d) of PVP (8.3 g/l) with the potential scan in negative (a,b) and positive (c,d) directions. Water/ 0.1 M KNO₃, $\nu = 100$ mV/s.

In this medium, like in many other media (Fedorenko *et al.*, 2015; Kokorekin *et al.*, 2017; Nasretdinova *et al.*, 2015a, 2015b, 2016, 2017, 2018; Yanilkin *et al.*, 2014a, 2015b, 2015c, 2016c, 2017e, 2017g), methylviologen (MV²⁺) is reduced harder than Ag⁺ in two stage to form stable radical cation(MV^{•+}) ($E_{C2} = -0.72$ V) and neutral diamine (MV⁰) ($E_{C3} = -1.06$ V) (Scheme 2) (Yanilkin *et al.*, 2016a).



Scheme 2. Reversible reduction of methylviologen

Earlier (Nasretdinova *et al.*, 2015a, 2015b; Yanilkin *et al.*, 2016a) it was shown that the radical cations of methylviologen efficiently reduce Ag⁺ ions. Therefore, the preparative mediated electroreduction of Ag⁺ was carried out at the controlled reduction potential of MV²⁺ to MV^{•+} ($E = -0.80$ V) in the presence of PVP at room temperature. The electrolysis conditions and the characteristics of the obtained NP are given in Table 1. For the experimental detection of the influence of the polymer chain length, identical concentrations of PVP with very different molecular masses of 40 000 D (PVP₄₀) and 1 300 000 D (PVP₁₃₀₀) were used. The concentration of PVP₄₀ was varied in the range from 0.03 to 8.30 g/l, and the concentration of PVP₁₃₀₀ was changed in the range from 0.50 to 8.30 g/l at the constant concentration of Ag⁺ ions. Ag⁺ ions were supplied to the solution *in situ* by dissolving the Ag-anode during electrolysis. A slight decrease in current occurs in the course of electrolysis (Table 1). In all cases, the amount of electricity theoretically necessary to generate Ag⁺ ions in a concentration of 1.5 mM

was passed. In all electrolysis experiments, the clear and colorless initial solution first became yellow, and then it turned brown. The consistency and color of the solution after completion of the electrolysis depended on the concentration of PVP. The solution was cloudy and black at low concentrations of PVP₄₀ (0.03 and 0.16 g/l) (Fig. 3). 30 minutes after the end of the electrolysis, the entire precipitate in the solution settled on the walls of the cell, on the electrodes, bridge, and magnetic stirrer. After ultrasonic treatment, the precipitate again moved into the solution, but a certain amount of precipitate still remained on the cathode, as evidenced by an increase in its weight by 0.4 mg. At all other concentrations of PVP₄₀ and PVP₁₃₀₀, the solution after electrolysis was turbid and swamp (Fig. 4), the precipitate did not fall out and the cathode mass did not change during electrolysis.

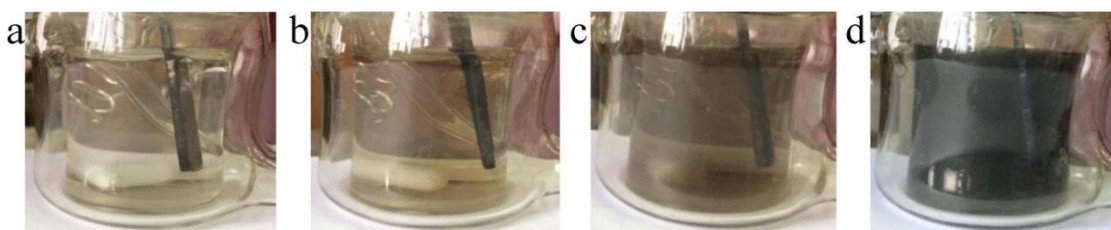


Figure 3. Photo of the electrolysis cell for the electrolysis No. 1, 2 for various amounts of electricity passed (%): 0 (a), 2 (b), 30 (c), 100 (d).

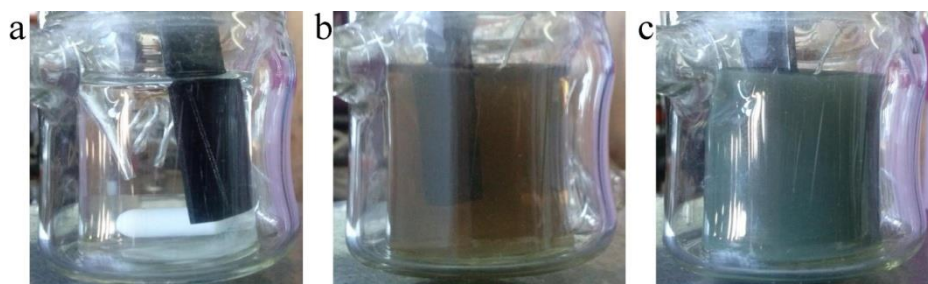


Figure 4. Photo of the electrolysis cell for the electrolysis No. 3-10 for various amounts of electricity passed (%): 0 (a), 30 (b), 100 (c).

A decrease in weight of the Ag-anode during electrolysis indicates its *in situ* dissolution. However, the weight loss is higher than it should be according to Faraday's law. And in general, with some exceptions, there is a general trend: the current yield ($CY = (m_{\text{theor}}/m_{\text{exper}}) \cdot 100\%$) of metal in the solution increases with increasing the PVP concentration (Table 1). The CV analysis of the solution obtained after electrolysis shows the absence of Ag^+ ions and the presence only of methylviologen in the initial concentration. The representative CV curve illustrating the foregoing is shown in Fig. 5. It is obvious that in the course of electrolysis, a quantitative methylviologen mediated reduction of electrochemically generated Ag^+ ions to form AgNP in the solution occurs. AgNP are also obtained as a result of the dispersion of the Ag-anode (Scheme 3). The contribution of this process increases with increasing the PVP concentration.

AgNP in the solution obtained after electrolysis were identified by CV (the adsorption peak of their oxidation) (Fig. 6), by UV-VIS (the absorption band (λ , Table 1) in the range of 400 ÷ 450 nm due to the surface plasmon resonance of AgNP) (fig. 7), and by TEM (Fig. 8). The shape and average size of AgNP were determined from the

TEM image, and the average size of AgNP with the PVP shell was estimated from the SEM image (Fig. 9). The presence of silver in NP was proved by microprobe element analysis (energy-dispersive spectra) (Fig. 8, 9).

Table 1. Conditions of methylviologen mediated electrosynthesis of AgNP and characteristics of the obtained particles.

exp. No	Stabilizer	C_{pvp} , g/l	Electrolysis parameters			Ag-anode		Characteristics of resulting NP			
			E, V vs. SCE	I, mA	Q, C	the mass loss, mg	CY, %	E_{A1} , V vs. SCE ^a	λ , nm ^b	Size of resulting NP, nm	
										SEM ^d	TEM ^d
1	PVP ₄₀	0.03	-0.80	2.8→2.5	2.90	3.4	106	0.40	^c	-	20±6
2	PVP ₄₀	0.16	-0.80	4.1→3.6	2.90	3.6	112	0.39	446 ^{c,d}	-	23±8
3	PVP ₄₀	0.50	-0.80	1.6→1.5	2.90	4.2	131	0.41	454 430 ^d	84±18	42±6
4	PVP ₄₀	1.00	-0.80	3.0→2.9	2.90	5.3	166	0.41	440 420 ^d	71±15	34±11
5	PVP ₄₀	1.80	-0.80	3.5→2.6	2.90	5.2	163	0.39	432 417 ^d	64±12	35±19
6 ^e	PVP ₄₀	8.30	-0.80	2.0→1.8	2.17	3.1	129	0.39	416 405 ^d	35±9	26±6
7	PVP ₁₃₀₀	0.50	-0.80	2.1→1.9	2.90	4.0	125	0.37	445 404 ^d	72±15	61±12
8	PVP ₁₃₀₀	1.00	-0.80	2.0→1.9	2.90	3.4	106	0.41	428 421 ^d	63±12	47±11
9	PVP ₁₃₀₀	1.80	-0.80	1.3→1.2	2.90	4.6	144	0.41	440 441 ^d	67±12	58±13
10	PVP ₁₃₀₀	8.30	-0.80	1.3→1.1	2.90	4.7	147	0.41	443 445 ^d	64±13	48±14

^aPotential of the AgNP oxidation peak; ^bWavelength of the AgNP absorption band; ^cWide band without the express maximum; ^dAfter particles isolation and subsequent dispersion in ethanol; ^e The data of (Yanilkina *et al.*, 2016a), in which the volume of the solution was 1.3 times smaller.

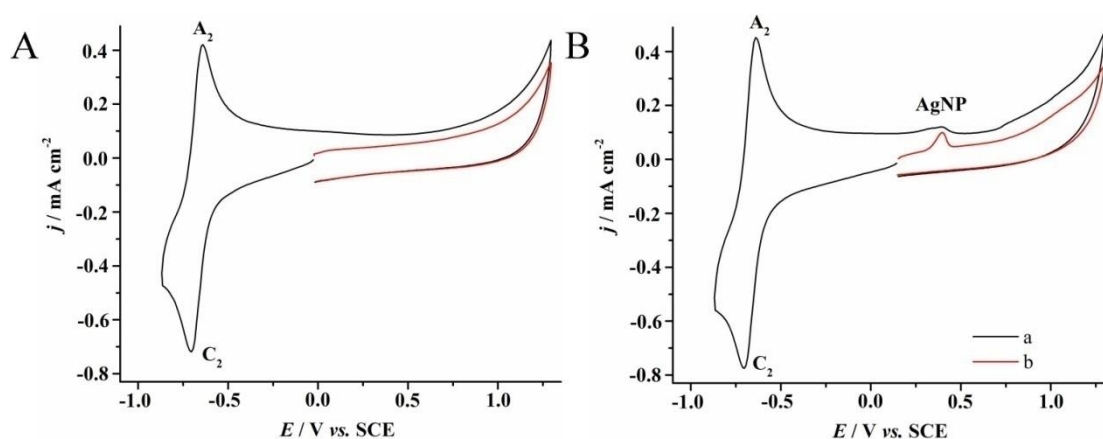
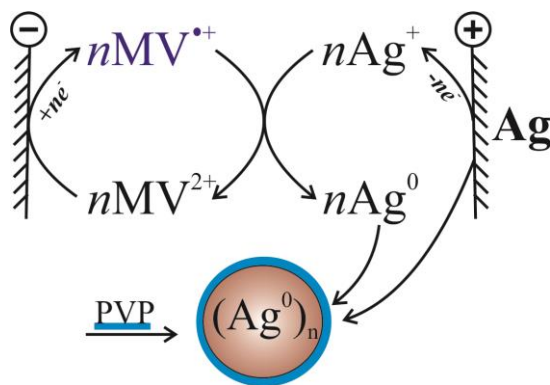


Figure 5. CV curves of the MV²⁺ (2 mM) – Ag-anode – PVP₄₀ (0.16 g/l) system before (A) and after (B) electrolysis No. 2 with the potential scan in negative (a) and positive (b) directions. Water/ 0.1 M KNO₃, $\nu = 100$ mV/s.



Scheme 3. Methylviolegen mediated electrosynthesis of AgNP in single compartment cell using soluble Ag-anode.

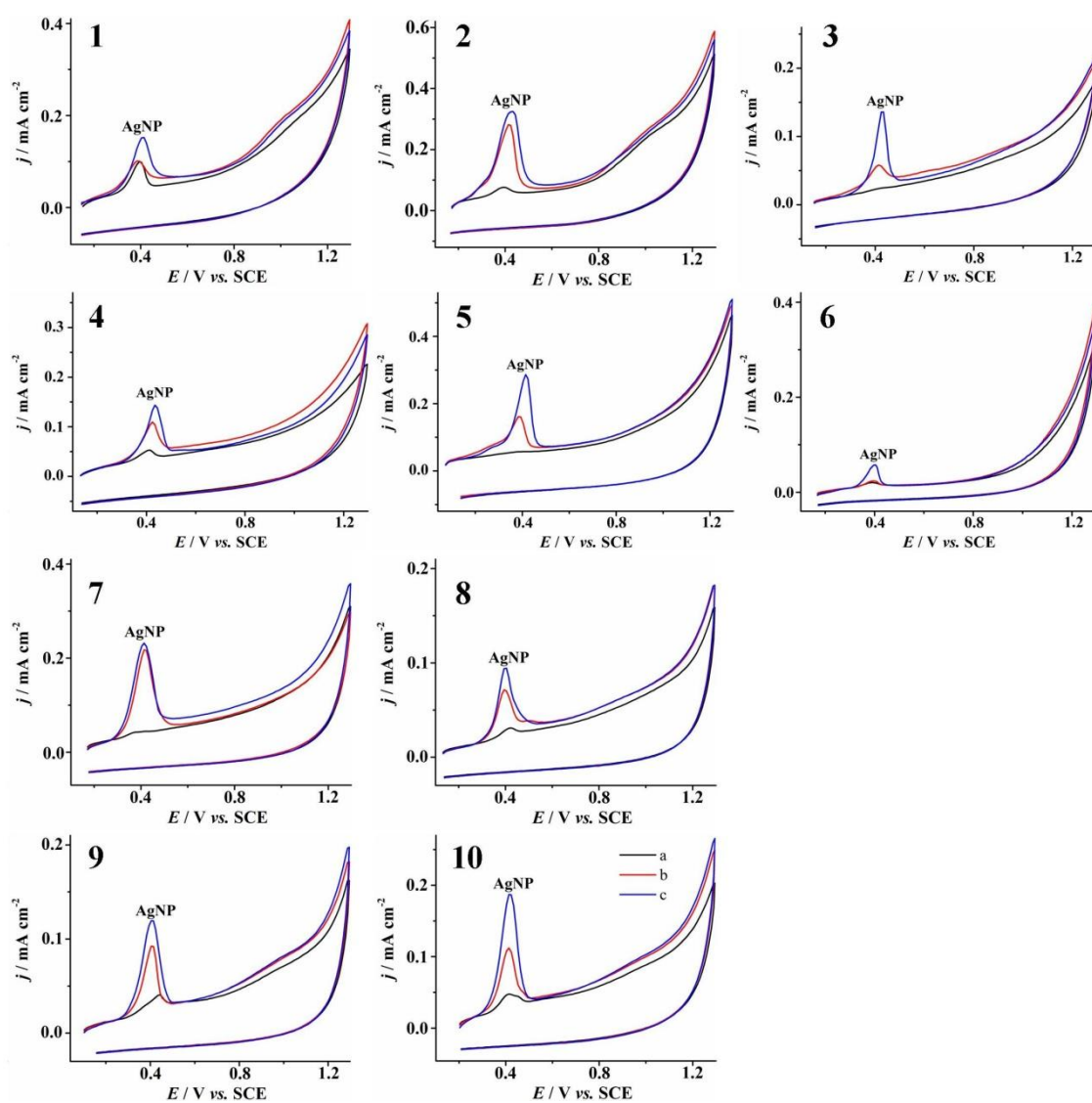


Figure 6. CV curves of AgNP after the electrode exposure without stirring and without applying a potential in the solution obtained after electrolyses No. 1-10 for various periods, s.: 5 (a), 60 (b), 180 (c). $v = 100 \text{ mV/s}$.

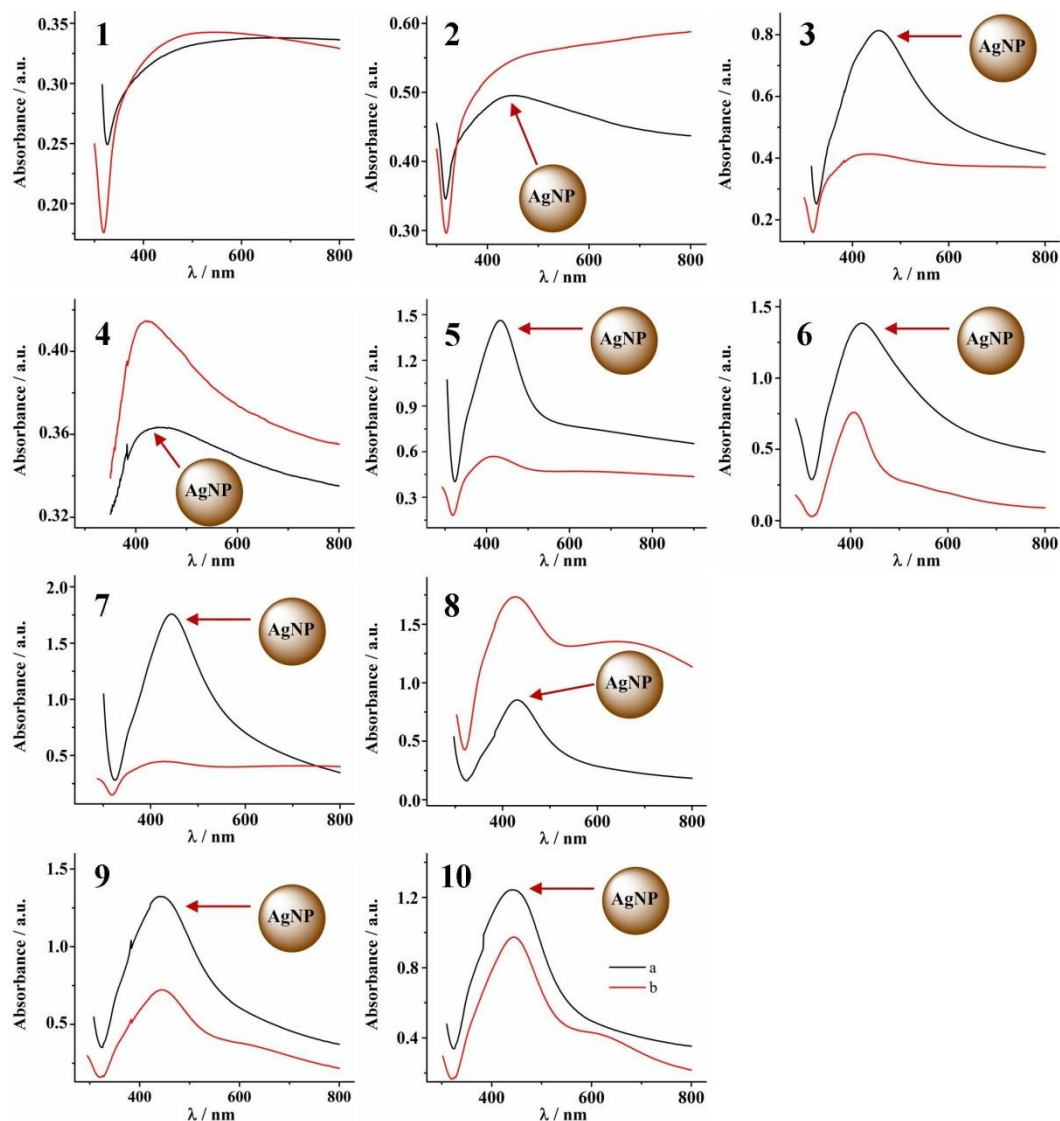


Figure 7. UV-VIS spectra of AgNP obtained by the electrolyses No. 1-10: in the solutions after electrolysis (a) and NP isolated and then dispersed in ethanol (b).

The set of results obtained leads to the following conclusions. AgNP are formed in the solution bulk in all electrolyses. They are stabilized in the PVP shell, have the form of imperfect spheres, their size is varied depending on the concentration and nature of PVP. PVP₄₀ in the amount, at which the concentration of monomer units is comparable to or lower than the concentration of Ag⁺ ions (≤ 1.5 mM), is unable to fully stabilize obtained AgNP. Therefore, only a certain part of the obtained AgNP is stabilized in the form of separate particles in the PVP shell. The rest of AgNP agglomerates forms larger particles of different sizes and shapes, including hexagonal. These large particles precipitate in the solution after electrolysis. Therefore, electrosyntheses were not performed at low concentrations of PVP₁₃₀₀. At high concentrations of PVP in the range from 0.50 to 8.30 g/l, the average size of metal particle decreases with increase in the concentration of both stabilizers. The results of the experiment No.8 fall out of this general trend for some unknown reason (Table 1). The AgNP size in the presence of PVP₄₀ is noticeably less than in the presence of

PVP₁₃₀₀ at all equal concentrations of PVP, i.e. PVP with a shorter polymer chain length stabilizes smaller metal particles. Thus, it is possible to control the average size of the resulting AgNP in a sufficiently wide range from 26 ± 6 to 61 ± 12 nm by varying the concentration in the indicated range.

MNP are in themselves thermodynamically unstable due to excess surface energy, and in the absence of stabilizers, they undergo agglomeration (aggregation). The resulting AgNP should be completely coated with PVP to stabilize them. Assuming equal metal mass, the total surface of NP is the larger, the smaller the particle size. Accordingly, more PVP is required for full encapsulation of AgNP of a smaller size in the PVP shell. From this point of view, decrease in the AgNP size with increasing the PVP concentration seems quite logical. However, the expected formation of monodisperse particles due to uniform distribution of PVP between AgNP does not occur. Polydisperse particles are obtained at the PVP concentrations from 0.50 to 8.30 g/l, and only a part of AgNP is stabilized in the PVP shell at lower concentrations. With regard to the effect of the nature of PVP on the particle size, apparently, long PVP₁₃₀₀ molecules are not able to stabilize small AgNP, i.e. there must be a certain correspondence between the polymer chain length and the size of AgNP stabilized by them.

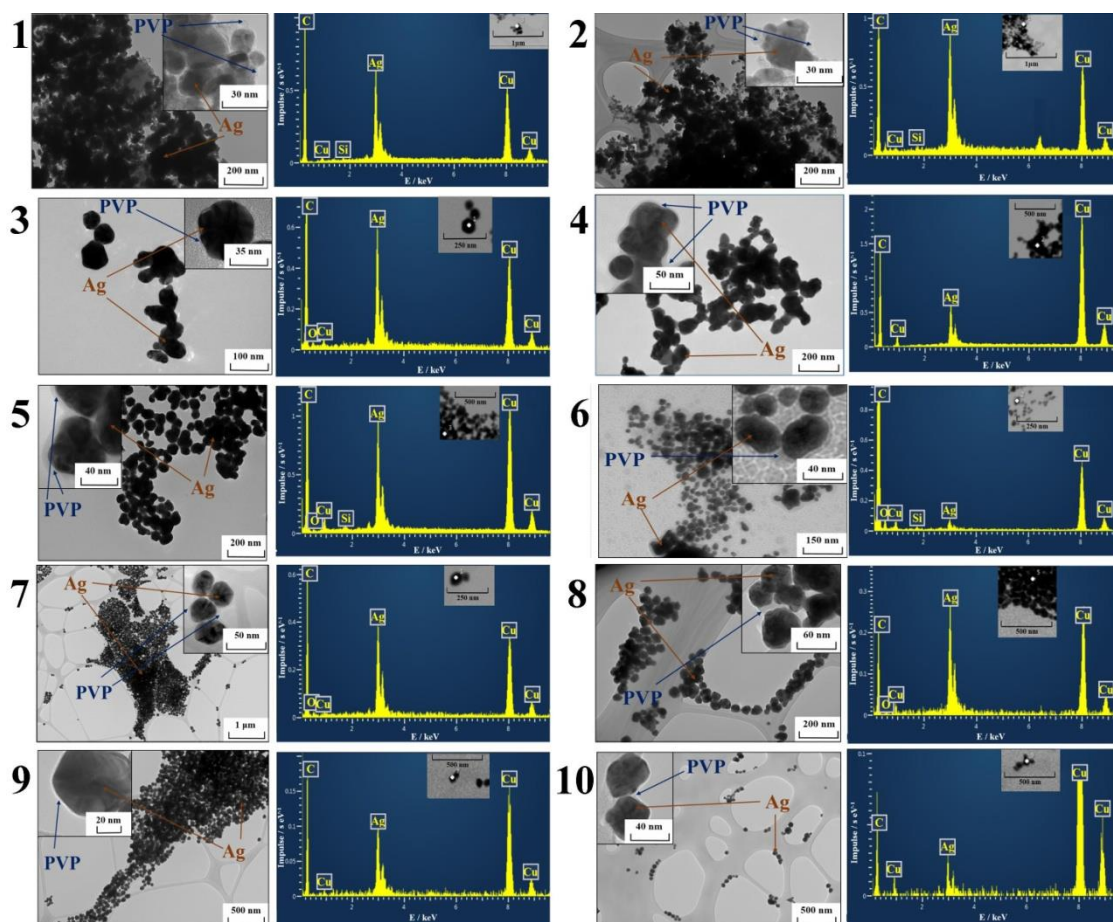


Figure 8. TEM images and energy-dispersive spectra of AgNP obtained by the electrolyses No. 1-10.

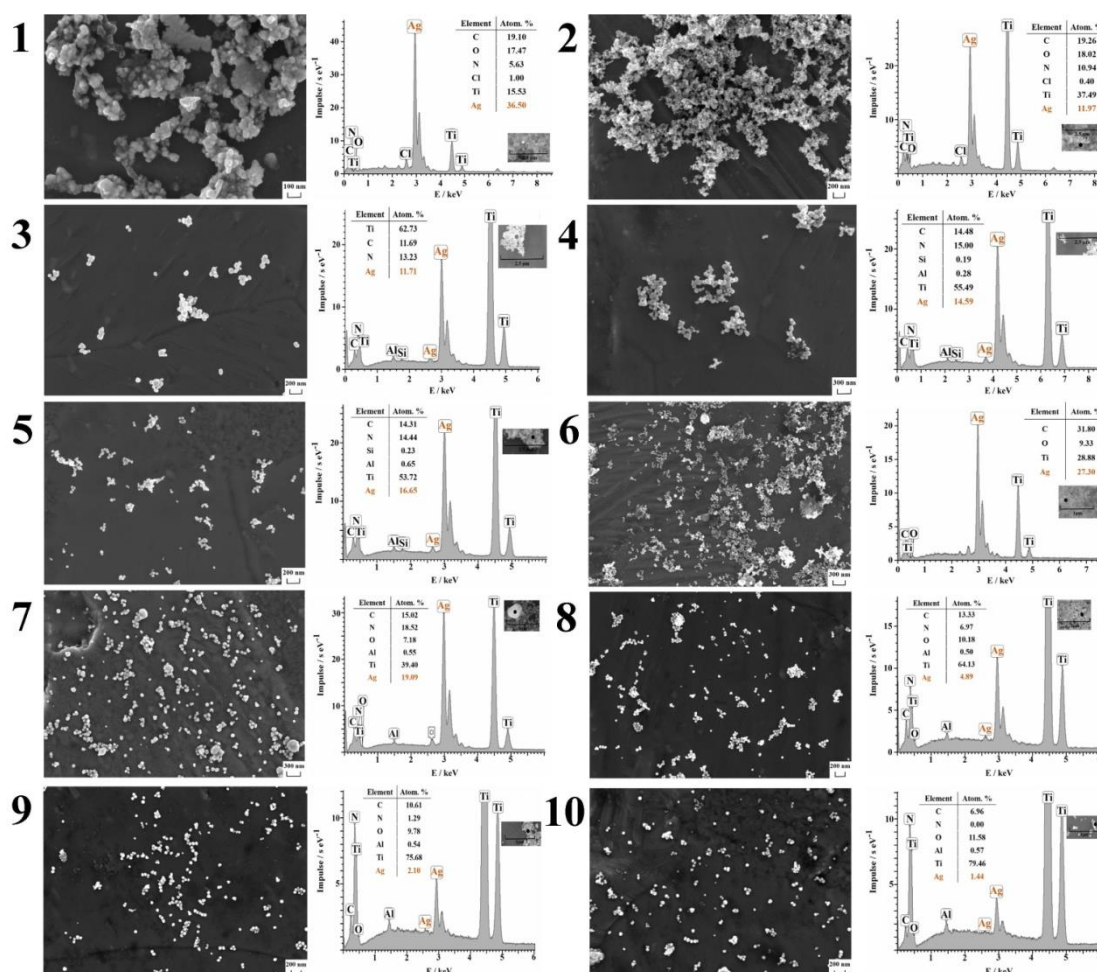


Figure 9. SEM images and energy-dispersive spectra of AgNP obtained by the electrolyses No. 1-10

4. Conclusion

To detect the influence of chain length and concentration of PVP on the AgNP size, methylviologen mediated electroreduction of Ag^+ ions *in situ* generated in the course of the Ag-anode dissolution was carried out at the potentials of the $\text{MV}^{2+}/\text{MV}^{\cdot+}$ redox couple in a single compartment cell in water/ 0.1 M KNO_3 medium in the presence of different concentrations of PVP₄₀ and PVP₁₃₀₀. In the course of electrolysis, a quantitative reduction of Ag^+ ions to form AgNP in the solution bulk occurs. AgNP are also obtained as a result of the dispersion of the Ag-anode. The contribution of this process increases with increasing the PVP concentration. NP are stabilized in the PVP shell, have the form of imperfect spheres, their size is varied depending on the concentration and nature of PVP. The total current yield of AgNP (106 ÷ 163%) increases and the particle size decreases with increasing the PVP concentration. The AgNP size in the presence of PVP₄₀ is noticeably less than in the presence of PVP₁₃₀₀. Thus, it is possible to control the average size of the resulting AgNP in a sufficiently wide range from 26 ± 6 to 61 ± 12 nm by varying the nature of stabilizer and its concentration in the indicated range.

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