Electrochemical synthesis of silver nanoparticles in poly(vinyl alcohol) solution

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Abstract: In this work, silver/poly(vinyl alcohol), Ag/PVA, colloidal dispersions were obtained by electrochemical reduction of Ag^+. The electrochemical synthesis of silver nanoparticles in aqueous solutions of 5 and 10 wt. % PVA, containing 0.1 M KNO_3 and 3.9 mM $AgNO_3$, was performed at a constant current density of 25 mA cm^{-2} for a synthesis time of 10 min. The presence of silver nanoparticles was confirmed by UV–Vis spectroscopy. Cyclic voltammetry analysis and FT-IR spectroscopy indicated interactions between the silver nanoparticles and the PVA molecules. TEM analysis confirmed the spherical shape of the obtained silver nanoparticles, with a mean diameter of 15±9 nm.

Keywords: electrochemical synthesis; PVA; silver nanoparticles.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a widely used synthetic polymer. The benefits of its use lie in its properties: non-toxicity, water-solubility, biocompatibility, biodegradability and excellent mechanical properties.[1–6] In addition, its low price and wide availability makes PVA a polymer of choice in a large number of applications.[6] The regular linear structure of PVA with a large number of side hydroxyl groups on the main chain suggests excellent hydrophilicity and reactivity. Solubility of PVA in water permits the formation of transparent films by evaporating the water from the aqueous solution. PVA in the form of flexible water-soluble films is used, mostly for its oxygen barrier effect, *e.g.* in paper coatings, textile sizing and in packaging.[4] The functional modification of PVA molecule widened its use by making different adsorbents, such as ion-exchange films, hydrogels and metal-complexion membranes.[2] Different processing technologies

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are used for the enhancement of the chemical stability, biodegradation resistance and mechanical strength by chemical and physical crosslinking, and hardening modifications.[4,7–9] Hydrogels made of PVA have recently become attractive as matrices for the repair and regeneration of several types of tissues and organs in the fields of tissue engineering and regenerative medicine.[7–16] The significant swelling capacity of PVA hydrogels, that enables the absorption of exudates generated during the process of wound healing, makes them adequate biomaterials for wound dressings.[12,17–20]

Nanosized structures of silver, ranging from 1 to 100 nm, have been in the focus of investigations over several decades. Due to the maximization of the total surface area of the nanoparticles that leads to the highest values of the activity to weight ratio, the properties of silver nanoparticles (AgNPs) are significantly different from those of the bulk metal. As a result, AgNPs have found applications in various fields, first in medicine.[21–26] For years, silver products have been used as antimicrobials on different wounds, such as burns, traumas and diabetic ulcers. Silver toxicity implies complex activity against multiple components of bacterial cell metabolism, including damage to the bacterial cell wall (membrane permeability leads to changes in the cellular structure), blockage of systems responsible for transport and enzymatic activity (*e.g.* respiratory cytochromes), alteration of proteins as well as binding of microbial DNA and RNA, thus preventing transcription and division of bacteria.[27,28] This combined effect makes bacteria unable to become immune to the silver antimicrobial function, which is not the case with antibiotics.

High purity of the metal particles as well as the possibility of precise particle size control can be obtained by electrochemical synthesis, by adjusting the current density or applied potential.[26,29] Without the necessity of a large number of different chemical as used in conventional chemical methods, this approach is especially attractive for biomedical applications.

In this work, silver nanoparticles were electrochemically synthesized by reduction of silver ions, for the first time using PVA as a capping agent. The effect of the PVA concentration on the amount and size of AgNPs was investigated, as well as the interaction between the silver nanoparticles and PVA. The advantages of this procedure are especially attractive for biomedical applications: all steps of synthesis are clean, few chemicals are used, and the obtained Ag/PVA colloid solution is biocompatible and biodegradable.

EXPERIMENTAL

Materials

The following chemicals were utilized in this work: fully hydrolyzed PVA powder ("hot soluble", M_w = 70000–100000 g mol^{-1}, Sigma, St. Louis, MO, USA), $AgNO_3$ (M. P. Hemija, Belgrade, Serbia), KNO_3 (Centrohem, Stara Pazova, Serbia) and $Ca(NO_3)_2 \cdot 2H_2O$ (Alkaloid, Skopje, FYR Macedonia). In all experiments, ultra pure water from a Milli-Q system

(Millipore, Billerica, MA, USA) was used as well as N_2 gas of high purity (99.5 %, Messer Tehnogas a.d., Belgrade, Serbia).

Synthesis of Ag/PVA colloid dispersions

Ag/PVA colloid dispersions were obtained by electrochemical reduction of silver ions in PVA solutions. PVA powder was first dissolved in hot water and, after cooling to room temperature, mixed with KNO_3 and $AgNO_3$ solutions to obtain final concentrations of 5 and 10 wt. % PVA, 0.1 M KNO_3 and 3.9 mM $AgNO_3$. The electrochemical synthesis was performed galvanostatically in an electrochemical cell containing 50 cm^3 of the solution using a Reference 600 Potentiostat/Galvanostat/ZRA (Gamry Instruments, Warminster, PA, USA). Two Pt plates (9 mm×10 mm) were employed as the working and counter electrodes, and a saturated calomel electrode (SCE) was used as a reference electrode. The applied current density was 25 mA cm^{-2} and the synthesis time was 10 min. The synthesis was performed under continuous stirring; N_2 was introduced into the solution for 20 min prior to the synthesis, followed by continuous N_2 flow over the solution during the synthesis.

Characterization of Ag/PVA colloidal dispersions

UV–Vis spectroscopy. UV–Vis spectroscopy was employed to confirm the presence of AgNPs in the Ag/PVA colloidal dispersions (UV-3100 spectrophotometer, Mapada, Japan). The wavelength was scanned between 200 and 1000 nm.

Cyclic voltammetry. Cyclic voltammetry investigations of a Pt electrode were performed in 10 wt. % PVA solution and in the Ag/PVA colloidal dispersion (10 wt. % PVA) using two platinum electrodes (9 mm×10 mm) as the working and counter electrodes, and a saturated calomel electrode (SCE) as the reference. Cyclic voltammetry was performed using Reference 600 potentiostat/galvanostat/ZRA (Gamry Instruments, Warminster, PA, USA). The measurements were recorded at a scan rate of 50 mV s^{-1}, in the potential region from −1 to 1 V *vs*. SCE, starting from the open circuit potential, E_{ocp}. All potentials are given *versus* the SCE, and the plotted voltammograms are stationary ones.

Fourier transform infrared (FT-IR) spectroscopy. The IR spectra were recorded on PVA and Ag/PVA thin films that were obtained by evaporating the solvent from 10 wt. % PVA solution and the Ag/PVA colloid dispersion (10 wt. % PVA). A Thermoelectron Corporation Nicolet 380 FT-IR spectrophotometer, operating in ATR mode, was used.

Transmission electron microscopy. Transmission electron microscopy of the Ag/PVA colloid dispersion (10 wt. % PVA) was performed using a 100 CX Electron Microscope (JEOL Ltd., Tokyo, Japan) operated at 100 kV, in order to examine the size and shape of the Ag nanoparticles. Samples for TEM analysis were prepared by deposition of a diluted Ag/PVA colloidal dispersion (1:4) on C-coated Cu grids (SPI Supplies/Structure Probe Inc., West Chester, PA, USA).

RESULTS AND DISCUSSION

UV–Vis spectroscopy

UV–Vis spectroscopy was employed to monitor the formation of the silver nanoparticles. Nano-sized silver exhibits a strong absorption due to the collective oscillation of the conduction electrons, after appropriate excitation by suitable radiation. This phenomenon is known as localized surface plasmon resonance (LSPR), which is highly dependent on the size and shape of the nanoparticles.[30]

The absorption spectra of pure 10 wt. % PVA solution and Ag/PVA colloid dispersions with 5 and 10 wt. % of PVA in the initial solution are shown in Fig. 1. The PVA spectrum did not exhibit an absorbance peak in the examined range of wavelengths. Both Ag/PVA colloidal dispersions exhibited absorption spectra with two bands peaking at around 400 and around 650 nm.
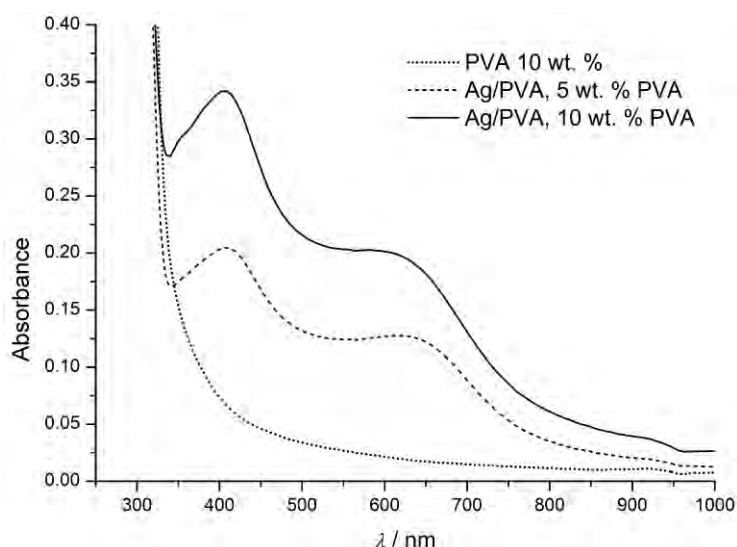

Fig. 1. Absorption spectra of 10 wt. % PVA solution and Ag/PVA colloidal dispersions with 5 and 10 wt. % PVA.

The first absorption peak at ≈400 nm confirms the formation of silver nano-particles.[31,32] The second absorption band peaking at nearly 650 nm can be explained by aggregation or agglomeration of the silver nanoparticles present in the colloidal dispersion.[33,34] The size and shape of the obtained silver nanoparticles will be further discussed in the next section where the results of TEM analysis are presented. The only difference between the spectra of Ag/PVA colloid dispersions obtained from initial solutions containing 5 and 10 wt. % PVA was in the absorbance intensity, where a higher absorbance was exhibited by the solution with the higher PVA concentration. This suggests that a higher concentration of silver nanoparticles was obtained with a higher concentration of PVA in the initial solution, since the concentration of the silver nanoparticles is proportional to the absorbance intensity.[34]

UV–Vis analysis was also used to determine the effect of PVA concentration on the amount and relative size of silver nanoparticles. The time dependences of the absorbance maximum, A_{max}, and the wavelength of the absorbance maximum, λ_{max}, are presented in Figs. 2 and 3, respectively. It can be seen in Fig. 2 that an increase in the PVA concentration increased the absorbance maximum,

indicating the greater amount of silver nanoparticles in Ag/PVA colloid dispersion. For both Ag/PVA colloid solutions, A_{max} increases up to the 20th day and then remained almost constant up to the 30th day, while a further increase in A_{max} is the consequence of gelation. It could be stated that the absorbance maximum was attained 20 days after the synthesis, when the growth of the silver nanoparticles terminated.
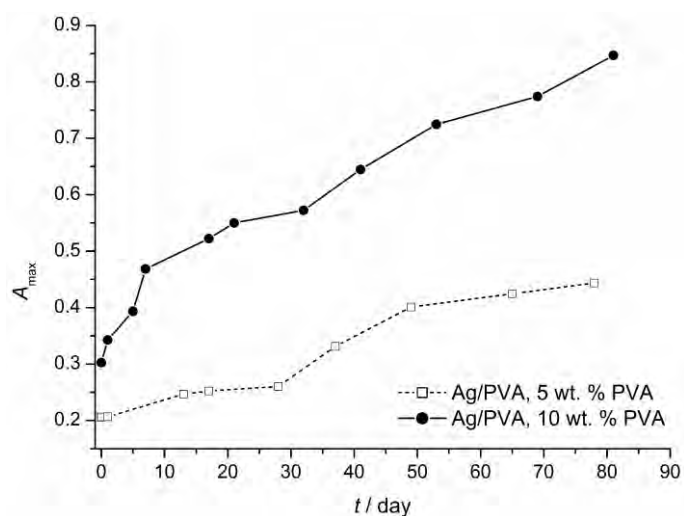

Fig. 2. Absorbance maximum, A_{max}, of Ag/PVA colloidal dispersions with 5 and 10 wt. % PVA as a function of time.
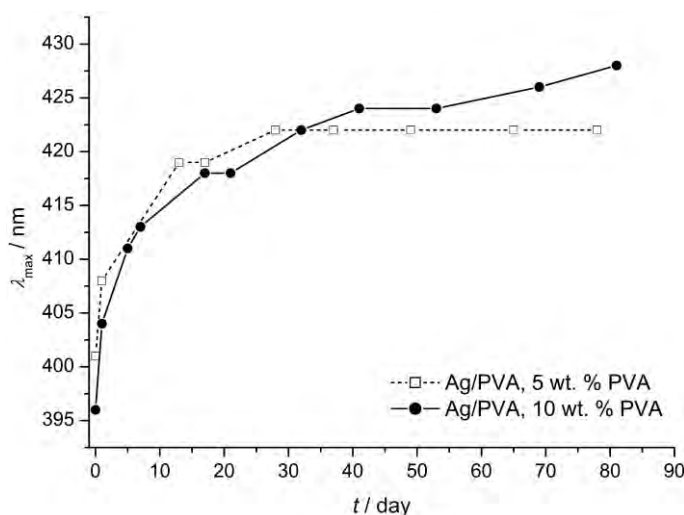

Fig. 3. Absorbance maximum wavelength, λ_{max}, of Ag/PVA colloid dispersions with 5 and 10 wt. % PVA as a function of time.

The time dependence of the wavelength of the absorbance maximum, λ_{max}, is presented in Fig. 3. It could be noticed that for both Ag/PVA dispersions, λ_{max} increased up to the 20th day, and then remained almost constant, and that the concentration of the PVA solution had no effect the size of the synthesized silver nanoparticles. This is in accordance with the previous assumption that the growth of silver nanoparticles terminated around 20 days after their synthesis.

Cyclic voltammetry

The cyclic voltammetry analysis of the Pt electrode was performed in 10 wt. % PVA solution and in Ag/PVA colloidal dispersion obtained from the initial solutions containing 5 and 10 wt. % PVA (Fig. 4). A better insight into the oxidation/reduction processes occurring in aqueous solutions of silver was obtained by comparison these cyclic voltammogram with those of the Pt electrode obtained in solutions containing 3.9 mM AgNO$_3$ and 0.1 M KNO$_3$.
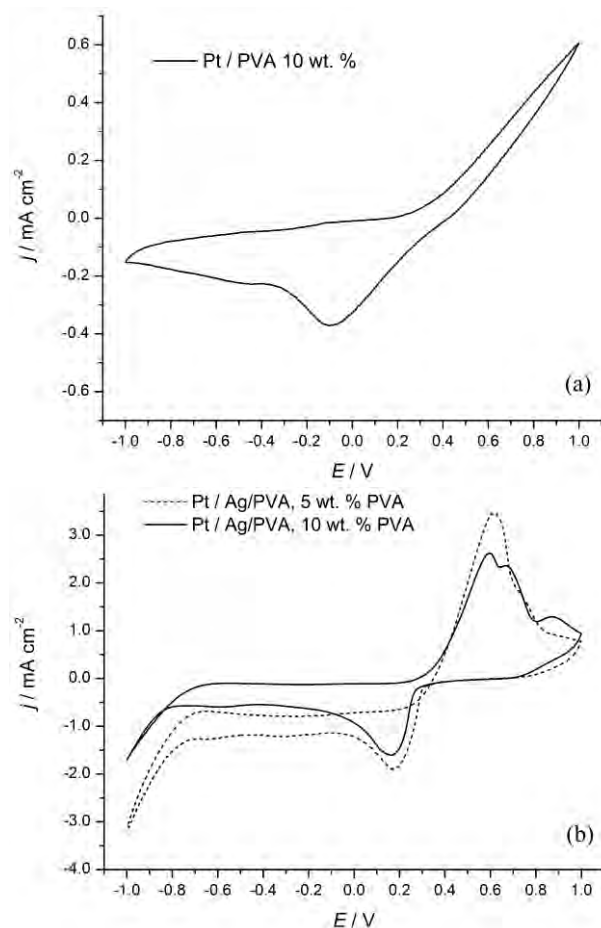

Fig. 4. Stationary cyclic voltammograms of a Pt electrode in a) 10 wt. % PVA solution and b) Ag/PVA colloidal dispersions with 5 and 10 wt. % PVA.

Cyclic voltammogram of the Pt electrode in 10 wt. % PVA solution (Fig. 4a) exhibited a broad cathodic peak at –100 mV, originating from reduction the Pt oxide formed during the anodic sweep. The anodic counterpart of this peak was not visible due to overlapping with the oxidation current at potentials more positive than 400 mV.

The stationary cyclic voltammograms of the Pt electrode in Ag/PVA colloid dispersions obtained from the initial solutions containing 5 and 10 wt. % PVA are shown in Fig 4b. In the Ag/PVA colloid solution obtained from the initial solution containing 5 wt. % PVA, the Pt electrode exhibited an anodic peak at around 611 mV, which originated from the oxidation of the Ag particles. This is connected with the oxidation/reduction processes of silver in the solution[24] where the appropriate pair of peaks appeared at 600 and 160 mV, respectively, and the minimal shifts towards more positive potentials (611 and 165 mV) could be the effect of the influence of the polymer molecules present in the solution. A small broad anodic peak appeared at around 870 mV, probably due to the oxidation of free Pt surface. The cathodic counterpart for the Pt oxide formation was not seen. However, considering the intensities of the cathodic currents in the potential region –200–200 mV, the cathodic counterpart for the Pt oxide formation could be overlapped with the Ag^+ reduction peak.

In the case of the Ag/PVA colloid dispersion obtained from the initial solution containing 10 wt. % PVA (Fig. 4b), three anodic peaks are obvious, at around 595, 667 and 871 mV. The first two could be related to the different oxidation processes of the silver nanoparticles in the Ag/PVA colloidal dispersion, while the peak at around 871 mV is related with the Pt oxide, as mentioned earlier. Only one cathodic peak was observed, at 160 mV. The two anodic peaks suggest differences between silver species; one was even less susceptible for oxidation.[35] This could be explained bearing in mind the entrapment of silver nanoparticles by PVA molecules, which implies silver nanoparticles with enhanced stability were obtained. Moreover, the coordination between Ag nanoparticles and hydroxyl groups of PVA was confirmed by FT-IR measurements, which will be discussed in the next section. The results indicated two types of AgNPs in the Ag/PVA colloidal dispersion, *i.e.*, relatively free ones that are susceptible to oxidation, and those already bonded to PVA molecules, that are hence less reactive.

Since it was proved that a higher concentration of silver nanoparticles in Ag/PVP solution were synthesized from the initial 10 wt. % PVA solution (UV––Vis measurements) as well as more stable silver nanoparticles were formed (CV measurements), all further characterizations were performed on Ag/PVA solution synthesized using the 10 wt. % PVA solution.

Transmission electron microscopy

Ag/PVA colloid dispersion obtained under the chosen experimental conditions (10 wt. % PVA, $c(AgNO_3)$ = 3.9 mM, j = 25 mA cm^{-2}, t = 10 min) was

analyzed using transmission electron microscopy. The TEM microphotograph confirmed the spherical shape of the synthesized silver nanoparticles (Fig. 5a). The average diameter of the obtained silver nanoparticles was 15±9 nm (Fig. 5b). It is known from the literature[36,27] that nanoparticles of the obtained dimensions exhibit antimicrobial characteristics.
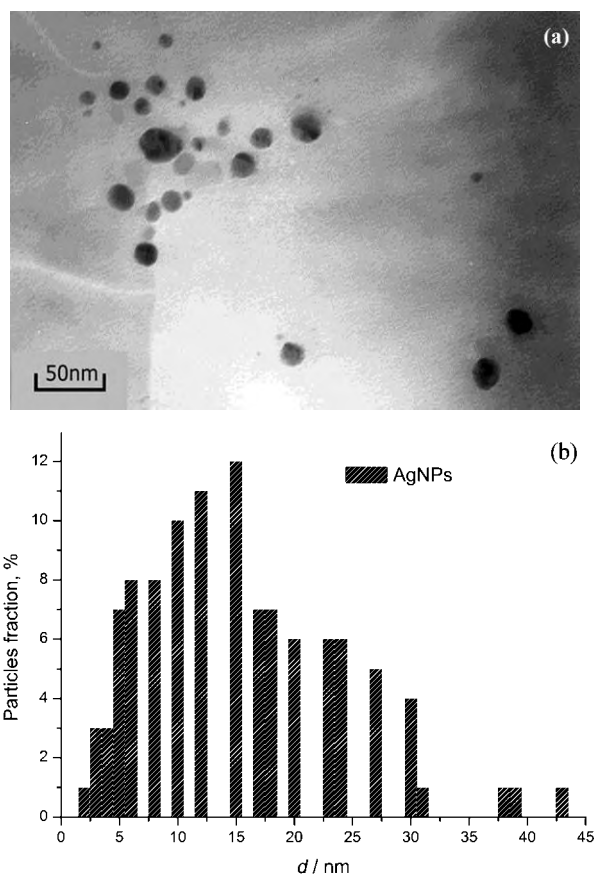

Fig. 5. a) TEM microphotograph of electrochemically synthesized silver nanoparticles in an Ag/PVA colloidal dispersion with 10 wt. % PVA and b) histogram of AgNPs particle size distribution.

Fourier transform infrared (FT-IR) spectroscopy

FT-IR measurements were performed on pure PVA and Ag/PVA thin films in order to determine the type of interactions between the PVA molecules and the silver nanoparticles. Thin PVA and Ag/PVA films were obtained by solvent evaporation from 10 wt. % PVA solution and Ag/PVA colloid dispersion obtained from the initial solution containing 10 wt. % of PVA, respectively (Fig. 6, Table I). The spectrum of the pure PVA exhibited characteristic peaks associated with poly(vinyl alcohol). A typical strong hydroxyl band for the –OH stretching vibration was observed at 3251 cm^{-1};[38] a band originating from C–H alkyl stretch-

ing was observed at a wavenumber of 2985 cm^{-1}.[39] Absorption peak originating from carboxyl stretching band (C–O) was verified at a wavenumber of 1141 cm^{-1}. The vibration band in the region between 1090 and 1150 cm^{-1} was attributed to the crystallinity of the PVA,[39] considering that PVA is a semi-crystalline synthetic polymer.[40]
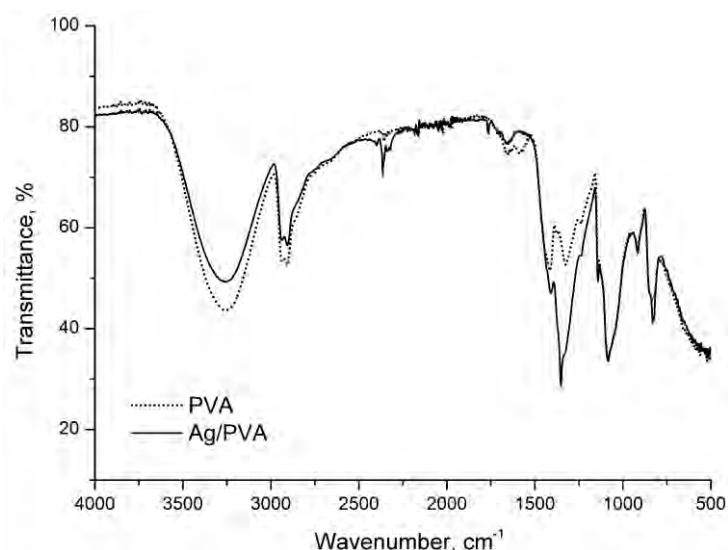

Fig. 6. IR Spectra of PVA and Ag/PVA thin films (PVA content in the initial solutions: 10 wt. %).

TABLE I. Wavenumbers of the characteristic bands and corresponding assignments for PVA and Ag/PVA thin films

Wavenumber (cm^{-1})		Assignment[38-46]
PVA	Ag/PVA	
3251	3253	–OH Stretching vibration
2937	2939	Asymmetric CH$_2$ stretching and aliphatic C–H stretching vibrations
–	1763	C=O Stretching of acetyl groups
1658	1650	Asymmetric and symmetric stretching vibration of –COO
1581	–	C=C Stretching vibration band
1414	1408	Weak –OH band vibration
1377	1352	–OH In plane coupling with C–H wagging
1325	–	
1238	1238	C–C Stretching vibration
1142	1142	Symmetric C–C stretching
1082	1084	C–O Stretching vibration of secondary alcohols
916	916	Symmetric C–C stretching
833	831	C–H rocking vibration

The IR spectrum of the Ag/PVA thin film exhibited a few differences compared to that of the pure PVA. Important changes were observed for the bands peaking at 1377 and 1325 cm^{-1} (in the PVA spectrum) and 1352 cm^{-1} (the in Ag/PVA spectrum). The strong band peaking at 1377 cm^{-1} is the result of the coupling of the –OH in-plane vibration with the C–H wagging vibrations. The increase in the intensity of the band at 1377 cm^{-1}, along with a slight shift of the band position (to 1352 cm^{-1} in the Ag/PVA spectrum), and the disappearance of the band peaking at 1325 cm^{-1} upon incorporation of Ag nanoparticles, suggests interaction between the AgNPs and the –OH groups of the PVA molecules through the decoupling between the corresponding vibrations. These results are in accordance with the results obtained from cyclic voltammetry, which indicated that PVA interacts with silver nanoparticles. As noted, there are two types of nanoparticles bonded with the PVA molecules, one which is more reactive, peaking at more negative values of the potential, and the other one, peaking at more positive values of the potential and thus more stable. Similar results were reported for alginate[26] and PVP.[24]

CONCLUSIONS

In this work, an electrochemical procedure was employed for the production of Ag/PVA colloidal dispersions with different concentrations of PVA. It was found using UV–Vis spectroscopy, that increasing PVA concentration in the initial solution increased the concentration of electrochemically synthesized AgNPs. Growth of the silver nanoparticles terminated around 20 days after the synthesis and their size remained almost constant up to the 30th day. The possibility of the use of PVA for the electrochemical synthesis of silver nanoparticles, as an adequate capping agent, was confirmed by cyclic voltammetry and IR spectroscopy, since the hydroxyl groups from PVA molecules coordinated with the Ag nanoparticles, making them more stable during a prolonged period. The obtained AgNPs were spherical, with a mean diameter of 15±9 nm, determined by TEM analysis. Thanks to the clean and simple procedure, electrochemically synthesized Ag/PVA colloidal dispersions could be utilized for the production of Ag/PVA hydrogels in different forms (thin films, discs and sheets), which could be used for antimicrobial treatments in biomedicine due to the release of AgNPs.

И З В О Д

ЕЛЕКТРОХЕМИЈСКА СИНТЕЗА НАНОЧЕСТИЦА СРЕБРА У РАСТВОРУ
ПОЛИ(ВИНИЛ АЛКОХОЛА)

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У овом раду показано је добијање колоидних дисперзија сребро/поли(винил алко-
хол), Ag/PVA, електрохемијском редукцијом Ag^+. Електрохемијска синтеза наночестица
сребра у воденим растворима поли(винил алкохола) са 5 и 10 мас. % PVA, који су садр-
жали 0,1 M KNO_3 и 3,9 mM $AgNO_3$, вршена је при константној густини струје од 25
mA·cm^{-2} у трајању од 10 min. Присуство наночестица сребра потврђено је ултраљубичас-
том и видљивом спектроскопијом. Цикличном волтаметријом и инфрацрвеном спектро-
скопијом показана је интеракција између наночестица сребра и молекула поли(винил
алкохола). Анализом трансмисионе електронске микроскопије је потврђено да су доби-
јене наночестице сребра сферног облика, пречника 15±9 nm.

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