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SYNTHESIS AND CHARACTERISATION OF SILVER NANOPARTICLES IN THE PRESENCE OF PVA AND TANNIC ACID

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Importanța nanoparticulelor metalice este dată de performanțele lor magnetice, electronice şi optice. Ca urmare a proprietăților specifice, ele au multe aplicații ca biosenzori şi catalizatori în biomedicină şi in domeniului mediului. Scopul acestei lucrări este prezentarea metodei de obținere şi analiză a filmelor polimerice pe bază de Ag/alcool polivinilic/acid tanic. Nanoparticulele de Ag au fost preparate prin reducerea $AgNO_3$ utilizând diferiți agenți de reducere (alcool polivinilic sau acid tanic) prin sinteză în câmp de microunde. Nanoparticulele de Ag (soluții şi film) au fost caracterizate prin spectroscopie UV – VIS , FTIR şi DLS (Dinamic Light Scattering).

The importance of metal nanoparticles is derived from their magnetic, electronic and optical performances. Due to their specific properties, they have many applications as biosensors and catalysts in biomedicine and environmental field. The purpose of this paper is to present the methods, the preparation and the characterization of polymeric films based on Ag/ Polyvinylalcohol (PVA) /Tannic acid. Silver nanoparticles have been prepared by reduction of silver nitrate using different reducing agents (PVA and/or tannic acid) in a microwave-assisted process. The silver nanoparticles (solutions and films) have been characterized by UV–VIS, FTIR spectroscopy and DLS (Dinamic Light Scattering).

Keywords: silver nanoparticle, microwave synthesis, tannic acid, polyvinyl alcohol

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1. Introduction

Silver metal nanoparticles are of significant interest in a wide range of applications: as catalysts, bactericides, optical and nonlinear optical materials. The synthesis of silver nanoparticles follows the colloidal route [1].

Two major methods used to prepare the metal–polymer nanocomposite materials are dispersion of separately prepared colloidal metal nanoparticle in the polymer matrix and colloidal metal nanoparticles synthesis inside the polymer matrix from a metal salt [2].

The second approach has become predominant these last years and a lot of work has been concerned with polyvinyl alcohol as matrix and silver nitrate as metal precursor. It has been shown that very different morphologies could be obtained as a function of the preparation conditions leading to different properties [3].

In microwave synthesis technique, a silver salt is reduced using a suitable reagent in the solution state and the silver nanoparticles generated are stabilized using appropriate capping agents. The various experimental factors such as the salt concentration, reducing and capping agent, reaction time and reaction temperature can be varied to control the formation and aggregation of the nanoparticles [4].

Recently, were reported *in situ* growth of metal nanoparticles in polymer films, by a simple protocol using silver nanoparticles and gold nanoplates embedded in polyvinyl alcohol (PVA) film [5].

The highlights of this method include the use of aqueous medium for the fabrication process, employment of the polymer itself as the reducing agent, mild thermal annealing for generating the metal, and *in situ* generation of the nanoparticles inside the polymer matrix which serves as the stabilizer as well. This protocol leads to supported as well as free-standing films. The metal/polymer ratio, reaction time and the heating conditions can be tuned in order to control the size and shape of nanoparticles [6].

Organic – inorganic hybrid nanomaterials have attracted great attention because of their potential to combine the features of organic with those of inorganic materials.

In this article, a microwave route for the synthesis of uniform silver nanoparticles using a single silver reduction step is presented.

Fine control over the nanoparticle's size and uniform distribution is achieved by varying the molar ration between $AgNO_3$/PVA and $AgNO_3$/tannic acid at different NaOH concentration reaction time, temperature and microwave power level.

2. Experimental

2.1. Materials

The reagents were of analytical purity and they were used without further purification: tannic acid ($C_{76}H_{52}O_{46}$) M_w = 1701.2 g/mol (Merck), $AgNO_3$ (Chimopar), NaOH (Chimopar), ultrapure water (conductivity 6 MΩ). PVA used has M_w 89.000-98.000 g/mol and hydrolysis degree 99 %.

Work solutions were prepared freshly at beginning of each experiments ($AgNO_3$ - 1 mmol, tannic acid - 6 mmol, pH = 8.5 by adding NaOH). The cleaning of laboratory glass vessels was carried out with oxidant mixture, prior to washing, for accuracy of the experiments.

2.2. Microwave reactor

All experiments were carried out in Biotage Initiator reactor, with multimode cavity and digital control of the process parameters: temperature, time, absorption level of the sample, transmitted power, stirring of sample. The volume of the reactor is 5 ml.

2.3. Analysis

The UV-VIS spectra were recorded using a UV-VIS spectrophotometer (SFM) model Jasco V550; literature values of the maximum UV-VIS absorption give λ = 400-430 nm for 2-20 nm silver nanoparticles.

Dynamic light scattering (DLS) analysis was performed on a Zetasizer Nano ZS type device from Malvern Instruments.

IR spectrum was recorded on a Jasco-FT-IR 4200 device.

3. Results and discussion

To make possible comparison of samples containing different Ag concentration a normalized absorption is calculated:

$$\mathrm{Abs_N} = \frac{A}{DF * \frac{c}{0.1}} \tag{1}$$

Where:

$\mathrm{Abs_N}$ – normalized absorption;
A – absorption of diluted solution;
c – silver concentration (mmol);
DF – dilution factor;

The first set of experiments was developed to determine the influence of silver concentration on the formation of nanoparticles using tannic acid as reducing agent. The reaction conditions and UV-VIS results are presented in table 1.

Table 1

Influence of silver concentration in formation of silver nanoparticles in the presence of TA. Reaction conditions: molar ratio TA/Ag=0.05 in the presence of NaOH (3 mmol), reaction temperature 90°C, reaction time 10 min.

Sample	Conditions		Results		
	Ag conc., mmol	DF	λ (nm)	A (cm^{-1})	Abs_N (cm^{-1})
P3	0.1	1	411	1.42	1.42
P3-PVA-3 Dil. 1/4	1	0.2	405	2.412	1.2
P3-PVA-6 Dil. 1/1	0.5	0.5	402	3.14	1.256

From this results, it is noted that, at low concentration of silver, transformation of ionic silver in nanoparticles is maximum (the highest value of normalized absorption is obtained).

In the second set of experiments the influence of NaOH was determined. The reaction conditions and UV-VIS results are presented in table 1.

Table 2

Influence of NaOH concentration in formation of silver nanoparticles in the presence of TA. Reaction conditions: $AgNO_3$ conc. =1 mmol, molar ratio TA/Ag=0.05 reaction temperature 90°C, reaction time 10 min.

Sample	Conditions				Results
	NaOH conc., mmol	DF	λ (nm)	A (cm^{-1})	Abs_N (cm^{-1})
AT 0.2 Na Dil. 1/2	0.1	0.33	415	1.91	0.573
AT 1 Na Dil. 1/2	1	0.33	420	3.18	0.954
AT 3 Na Dil. 1/2	0.5	0.33	400	3.76	1.128

The presence of NaOH is mandatory. Only in the presence of enough high concentration of NaOH (3mmol) a high level of normalized absorption is obtained. At lower concentration a smaller number of NPs are obtained (the normalized absorption is lower) and in the absence of NaOH the formation of NPs is stopped.

The following experiments were carried out in the presence of polyvinyl alcohol (PVA). The mass ratio PVA/$AgNO_3$ was 50:1. The silver nanoparticles are not formed if the NaOH is absent and the concentration of Ag has no influence. This observation is confirmed by UV-VIS spectra since no absorption peak is present in the characteristic region of nanoparticles (table 3).

Table 3

Influence of silver concentration in formation of silver nanoparticles in the presence of PVA. Reaction conditions: weight ratio PVA/Ag=50:1 reaction temperature 90°C, reaction time 10 min.

Sample	Conditions		Results	
	$AgNO_3$ conc., mmol	DF	λ (nm)	A (cm^{-1})
P3-PVA-1	0.1	1	271	0.06
P3-PVA-4	1	1	208 274	3.49 0.36
P3-PVA-7	0.5	1	210 272	3.30 0.225

The silver nanoparticles are formed when NaOH and PVA are present in the solution, but the normalized absorptions are much lower than the ones obtained in the presence of tannic acid (table 4).

Table 4

Influence of NaOH concentration in formation of silver nanoparticles in the presence of PVA. Reaction conditions: $AgNO_3$ concentration=1 mmol, weight ratio PVA/Ag=50:1 reaction temperature 90°C, reaction time 10 min.

Sample	Conditions		Results		
	NaOH conc., mmol	DF	λ (nm)	A (cm^{-1})	Abs_N (cm^{-1})
P3-PVA-4	-	1	208 274	3.49 0.36	-
P3-PVA-4 0.2mmol	0.2	1	211 278 427	3.33 0.2 0.008	-
P3-PVA-4 1 mmol	1	1	212 272 427	3.35 0.22 0.04	0.004
P3-PVA-4 3 mmol	3	1	207 267 427	3.47 0.26 0.23	0.023

The nanoparticles have been formed in similar quantities for the experiments in the presence of TA+PVA and NaOH as compared to the experiments in the presence of TA and NaOH (except the experiments at low Ag concentrations). At low Ag concentrations, the normalized absorption has the lowest value (table 5). A possible explanation for this behavior could be the stabilization of silver atoms on the polymeric chain of PVA. Only at relatively high concentration (> 0.5 mmol) the nanoparticles are formed.

Table 5

Influence of silver concentration in formation of silver nanoparticles in the presence of PVA+TA. Reaction conditions: molar ratio TA/Ag=0.05, weight ratio PVA/Ag=50:1 reaction temperature 90°C, reaction time 10 min.

Sample	Conditions		Results		
	Ag conc., mmol	DF	λ (nm)	A (cm^{-1})	Abs_N (cm^{-1})
P3-PVA-2	0.1	1	274 422	0.405 0.0998	 0.0998
P3-PVA-5 Dil. 1/4	1	0.2	407	2.35	1.175
P3-PVA-8 Dil. 1/1	0.5	0.5	403	3.07	1.228

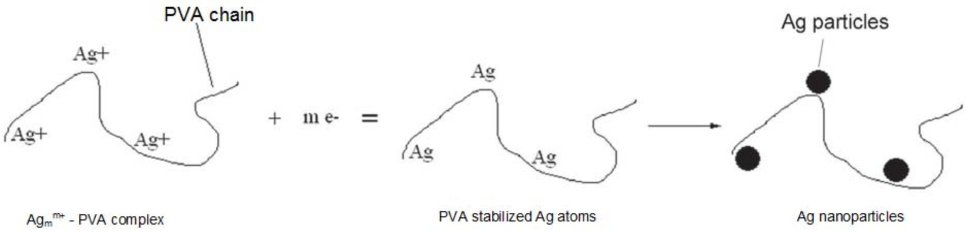

Fig. 1. Schematic illustration of the protective mechanism of PVA in microwave synthesis of silver nanoparticles

When comparing the FT-IR spectra of PVA, Ag-PVA and Ag-PVA-TA samples (Fig. 2) it can be observed that the formation of nanoparticles causes functional modification of the supporting matrix. This modification concerns the appearance of carbonyl groups (1654cm^{-1}) and changes in the symmetry of hydrocarbon chain in PVA (2850cm^{-1}) (see table 6).

Table 6

Main vibration determined in FT-IR spectra of PVA, Ag-PVA and Ag-PVA-TA films

Group	Wave number	Vibration	Functional group
C-OH	3292	OH stretching	Bounded and non bounded hydroxyl group
R-CH_2-R	2920	C-H stretching (as)	Aliphatic methylene group
R-CH_2-R	2850	C-H stretching (s)	Aliphatic methylene group
R-CO-R	1654	C=O stretching	Conjugated ketones
Aromatic ring	1563	Ring stretching	Aromatic ring

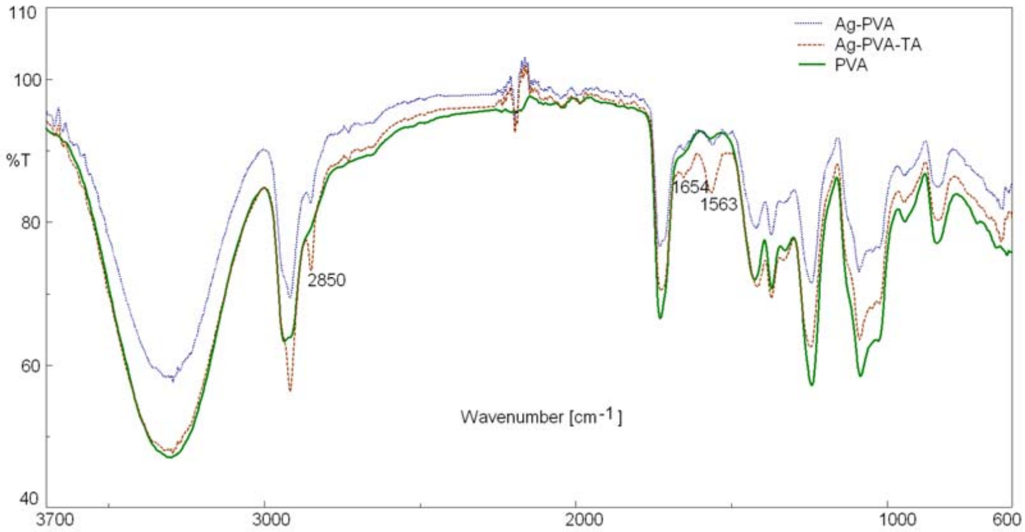

Fig. 2. FT-IR spectra of PVA, PVA containing Ag nanoparticles (Ag-PVA) and PVA containing Ag nanoparticles and TA (Ag-PVA-TA)

6. Conclusions

Silver nanoparticles were synthesized from aqueous solutions in the presence of PVA and/or TA. The synthesis process was developed into a microwave reactor (Initiator - Biotage). UV-VIS spectra were used in order to characterize the process of nanoparticles formation.

The influence of important parameters for the formation of Ag nanoparticles was investigated: Ag concentration, type of reducing agent (TA or/and PVA) and the concentration of NaOH. FT-IR spectra of the samples of PVA with/without nanoparticles evidenced modifications of the matrix due to the presence of nanoparticles.

These results may enable these material properties to be adjusted for their potential use in selected practical applications as sensor for different contaminants or for membrane in controlling of antimicrobial activity of water.

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