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Enhanced permeability of polyamide fabrics for silver nanoparticles via modification with boron nitride

I. V. Loktionova^{1,*}, P. V. Abakumov², A. P. Kuzmenko¹, A. I. Kolpakov¹, V. A. Mamontov¹,
E. A. Novikov¹ and L. P. Petrova¹

¹Southwest State University, Kursk, 305040 Russia

*E-mail: ms.chuhaeva@mail.ru

²Kursk State Medical University, Kursk 305041 Russia

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Polyamide membranes modified with boron nitride nanoparticles were studied for silver nanoparticle filtration. Atomic force microscopy revealed the formation of ordered nanolayers (particle size ~20 nm, roughness 24 nm). Raman spectroscopy confirmed the formation of chemical bonds while preserving the polyamide structure. The modified samples exhibited a high transmission coefficient (97–98%), exceeding that of the unmodified fabric by 35%, which is consistent with molecular dynamics simulation data. The obtained results demonstrate the potential of using modified polyamide membranes for efficient silver nanoparticle filtration.

Keywords: boron nitride; polyamide fabric; Langmuir films; magnetron films; membranes; nanoparticle filtration.

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Introduction

Filtration of colloidal solutions of metal nanoparticles, such as Ag, Au, Pt, Cu, Fe, and others presents a particular challenge in various applications of nanomaterials due to aggregation and interaction of the solutions with surfaces of filtering materials [1]. Polyamide membranes in filtration systems have found widespread use due to their availability, mechanical strength, stability, and durability in aggressive environments [2]. Modifying polyamide with nanoparticles of boron nitride (BN) featuring unique properties [3] enables the formation of ordered nanoporous structures with low hydrodynamic resistance and increased throughput, partly due to their resistance to swelling [4, 5]. Thus, paper [6] shows that introducing 5 wt.% BN into polyamide increases the average pore size from 50 nm to 80–100 nm and overall porosity by 15–20 %, creating branched nanochannels that enhance filtration

rates by 25–30 % [7, 8]. Incorporation of 3 wt.% BN reduces water flow resistance by 40% compared to unmodified polyamide [9], while introducing 5 % BN halves water absorption [10].

This reduces swelling, prevents pore clogging, and deformation of membrane cells, thus ensuring long-term stability of characteristics [7, 9]. Thus, modification of polyamide materials with boron nitride improves their throughput and operational stability.

This paper is aimed to research the features of filtering a colloidal solution of silver nanoparticles through PA6 fabric modified with boron nitride nanoparticles by the Langmuir-Blodgett method and magnetron sputtering.

Materials and Methods

Two methods were used to deposit nanofilms of boron nitride nanoparticles onto polyamide fabric (PA 6) with a thread diameter of

~400 μm , which consists of hundreds of thin filaments and has a smooth mesh surface. The Langmuir-Blodgett (LB) method was employed to form LB NF *h*-BN / PA 6 nanofilms (NF) on the surface of deionized water (18 M Ω -cm) under normal conditions using KSV Nima 2002 setup from a colloidal system (CS) of BN nanoparticles stabilized with stearic acid (SA). CS of 3- μl volume was applied onto the subphase surface. The transfer pressure was 20 mN/m. The high-frequency magnetron sputtering (MR) method was used to deposit MR NF BN / PA 6 nanofilms using MSU TM-MAGNA setup. A target of hexagonal boron nitride (*h*-BN) with a diameter of 100 mm was used. The working atmosphere consisted of nitrogen (0.25 l/h N₂) with the addition of argon (0.03–0.2 l/h Ar). The MR process was conducted during 3600 s at the power of 300 W. Prior to sputtering, the chamber was evacuated to 5×10^{-4} mmHg. The polyamide substrate was heated to 420 K.

The morphology of the Langmuir nanofilms was studied using scanning probe microscopy (SPM) SmartSPM (AIST-NT). Raman spectroscopy (RS) was performed using microspectrometer OmegaScope (AIST-NT) in $ZXX\bar{Z}$ geometry ($\lambda = 473 \text{ nm}$, from 170 cm^{-1}) and spectrometer LabRAM HR (Horiba) in $ZXYZ$ geometry ($\lambda = 532 \text{ nm}$, from 50 cm^{-1}), both with an identical spectral resolution of 0.8 cm^{-1} . The optical properties of CS were measured using spectrophotometer SF-2000 (range of 190–1100 nm). Filtration efficiency was determined by changes of the optical density of CS after passing it through original PA 6 fabric and modified samples (LB NF *h*-BN/PA 6 and MR NF BN/PA 6). To establish the reproducibility of findings, all experiments were conducted three times. The CS nanoparticle sizes were determined by small-angle X-ray scattering (SAXS) on SAXSess mc² diffractometer (Anton Paar, Cu K α , $\lambda = 0.154 \text{ nm}$, resolution $0.03\text{--}28 \text{ nm}^{-1}$). The colloidal system of silver nanoparticles was synthesized using the Kerry Lee method.

Filtration of Ag particles by the PA 6 matrix was modeled in Materials Studio 2020 using Forcite and Amorphous Cell modules. At first atomic-scale models of PA 6, water, and

silver were created, with geometry optimization performed using the Universal Force Field (including van der Waals and Coulombic interactions, Ewald summation method). Then, in Amorphous Cell, a periodic cell of an aqueous Ag solution (~10 wt.%) was formed, its structure was optimized, and molecular dynamics simulation was carried out (NVT ensemble, 298 K, 105 ps, time step 1.5 fs).

Findings and Discussion

Analysis of the formed nanostructured layer LB NF *h*-BN / PA 6 by SPM method revealed characteristic lateral particle sizes of ~20 nm (Fig. 1). The root-mean-square roughness of the LB NF *h*BN film layer on the PA 6 surface slightly increased and reached 24 nm (inset in Fig. 1). The roughness was measured at five different points on the membrane, and the calculated standard deviation from these measurements was 1.3 nm, which reflects surface variability and reliability of estimated mean values. A predominant orientation of particles between the primary fibers (filaments) of the fabric was observed, which is attributed to the action of capillary forces during formation of LB NF *h*-BN / PA 6.

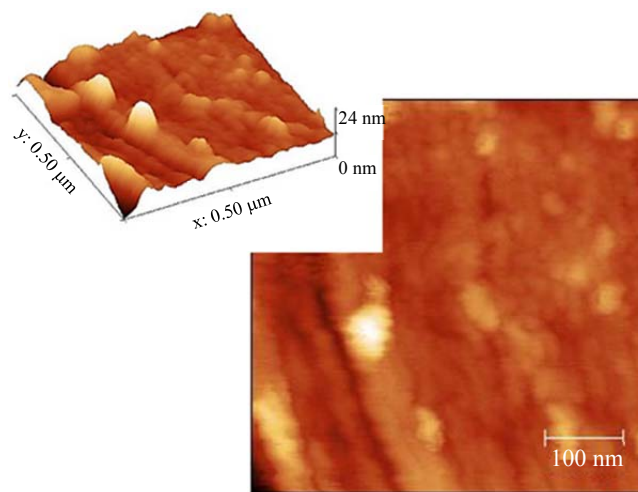


Fig. 1. SPM image of polyamide fabric modified with boron nitride nanoparticles. The inset shows the root-mean-square roughness of the LB NF *h*-BN film layer.

In $ZXYZ$ RS spectra of LB NF *h*-BN / PA 6 and MR NF BN / PA 6 samples, vibrational modes characteristic of both the polymer matrix

and deposited functionalized film were observed (Fig. 2). In the low-frequency region of the spectrum ($< 500 \text{ cm}^{-1}$), the LA mode of the boron-nitrogen lattice vibrations of *h*-BN at 149 cm^{-1} was excited. Its intensity was noted to grow after functionalization of *h*-BN with stearic acid. These changes in the surface polarizability of NF are due to the formation of chemical bonds between BN and carboxylate groups [11, 12].

The 478 cm^{-1} line corresponds to deformation vibrations of B–O bonds arising from partial oxidation of the *h*-BN surface or to low-frequency modes of amorphous BN (B–N–B bending vibrations). The 518 cm^{-1} signal can be attributed either to skeletal vibrations of the polyamide matrix (C–C–N–C deformation) or to defect modes of BN associated with nitrogen vacancies or boron atom substitutions [10].

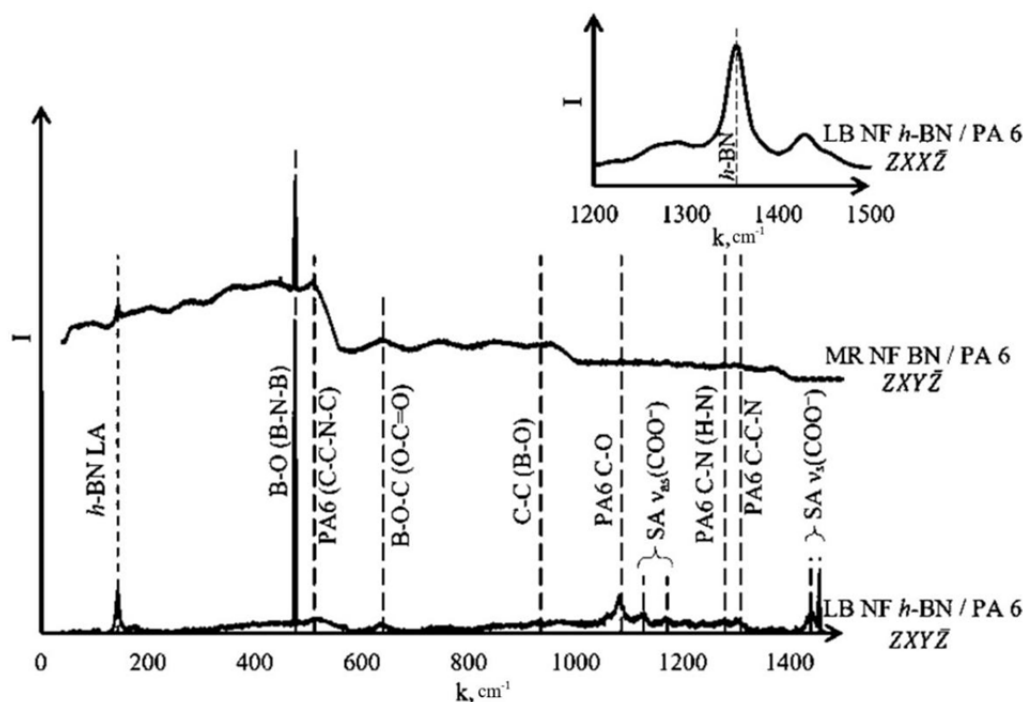


Fig. 2. Polarized ZXYZ Raman spectra for filter samples obtained by modifying PA6 with BN nanoparticles using LB and MR methods. The inset shows an example of the ZXXZ Raman spectrum for LB NF *h*-BN / PA 6 sample.

In the mid-frequency region ($500\text{--}1000 \text{ cm}^{-1}$), vibrations associated with the interaction between BN and stearic acid dominated. For instance, the peak at 643 cm^{-1} corresponded to deformation vibrations of carboxylate groups (O–C=O) in boron stearate, as well as to valence vibrations of B–O–C bonds, which confirmed the formation of chemical bonds between stearic acid molecules and BN surface. The signal at 930 cm^{-1} included contributions from valence vibrations of C–C in the polyamide chain and symmetric vibrations of B–O in boroxol structures (B–O–B), which could form due to partial hydrolysis of BN [13, 14].

In the $1000\text{--}1500 \text{ cm}^{-1}$ region, key modes were associated with carboxylate groups and amide structures. The peak at 1085 cm^{-1}

corresponded to valence vibrations of C–O in ether bonds of polyamide and antisymmetric vibrations of carboxylates ($\nu_{as}(\text{COO}^-)$). The doublet at $1132/1182 \text{ cm}^{-1}$ unambiguously identified the carboxylate group of stearic acid, where 1132 cm^{-1} corresponded to symmetric ($\nu_s(\text{COO}^-)$) and 1182 cm^{-1} to antisymmetric ($\nu_{as}(\text{COO}^-)$) vibrations. This indicated the deprotonation of acid and the formation of boron stearate. The peak at 1285 cm^{-1} is characteristic of amide III in polyamides (combination of C–N stretching and N–H deformation), which indicated that the structural integrity of the polymer matrix remained. The signal at 1310 cm^{-1} is related to crystalline phases of polyamide (ordered C–C–N segments) and deformation vibrations of CH_2 groups. Peaks at 1423 cm^{-1} and

1457 cm^{-1} corresponded to symmetric carboxylate vibrations ($\nu_s(\text{COO}^-)$) and deformation vibrations of CH_2 chains in polyamide and stearic acid, thus confirming that both components were present in the system in accordance with [11, 12]. The main peak for $h\text{-BN}$ at 1370 cm^{-1} in the non-polarized $\text{ZXX}\bar{\text{Z}}$ Raman $\text{ZXX}\bar{\text{Z}}$ -spectrum confirmed the successful deposition of nanoparticles onto PA 6 fibers (inset to Fig. 2).

The absorption spectrum of CS of silver nanoparticles exhibited two distinct but diffused maxima in the wavelength regions around 440 nm and 720 nm (Fig. 3).

These peaks corresponded to characteristic manifestations of the surface plasmon resonance (SPR), which arose from collective oscillations of

free electrons on the surface of metallic nanoparticles under the influence of the electromagnetic field of incident light [15]. The inset in Figure 3 also shows the SAXS results for this CS, which indicate its heterogeneous nature with nanoparticles sized 29, 56 and 100 nm. The conclusions drawn from the absorption spectra (Fig. 3) were supported by three well-defined peaks observed in the SAXS spectrum. Their occurrence indicated a discrete particle size distribution and good stabilization of CS. Similar polymodal SAXS spectrum structure is typical for complex CS. The symmetry and width of the dominant 56 nm peak suggested a high degree of CS monodispersity. The peak width at 100 nm indicated a significant spread of sizes within this group.

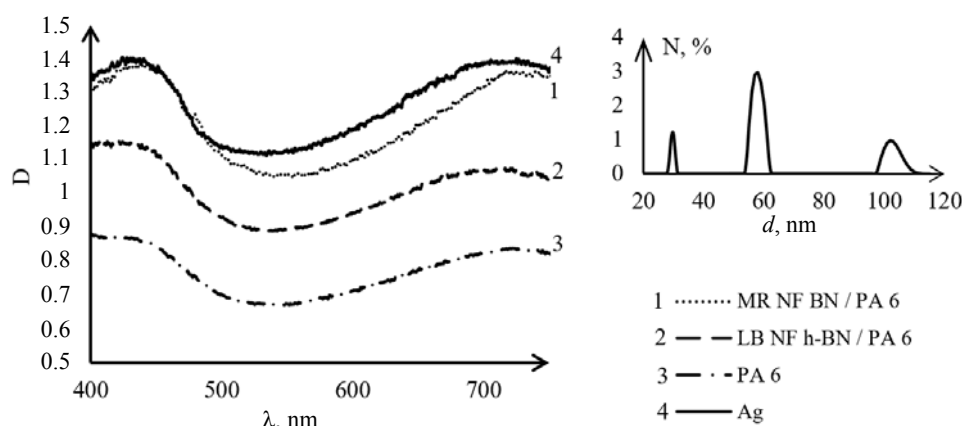


Fig. 3. Photometric spectra of CS of Ag nanoparticles before and after filtration. The inset shows the size distribution of silver particles (SAXS)

For CSs containing monodisperse spherical silver nanoparticles of small sizes (10–30 nm), SPR is typically observed in the blue part of the spectrum, around 400 nm. However, in this case, the main peak is shifted to the 440 nm region and is noticeably broadened, which allowed concluding about the polydisperse nature of the solution, i.e., the presence of particles sized within a broad spread. The shift toward longer wavelengths (red shift) could be due to the increased average particle diameter: as the size of silver nanoparticles grows (inset to Fig. 3 – 56 nm), SPR shifts to the region of lower energies with a longer wavelength, resulting in a bathochromic shift. The occurrence of SPR maximum in the 720 nm region indicated the formation of silver nanoparticle aggregates. According to paper [16], the interaction between their plasmon modes in such conditions was accompanied by additional absorption bands

typically occurring in the red or near-infrared region of the spectrum, and is attributed either to direct contact of particles or their close proximity in the CS solution – within the framework of so-called “plasmon coupling”. The decrease of optical density in the yellow and green regions of the spectrum could be caused by intensified light scattering by silver nanoparticle aggregates with sizes over 100 nm.

According to the Lambert-Beer-Bouguer law, optical density D is directly proportional to concentration c of CS. Therefore, dependence $D(\lambda)$ in Figure 3 is unambiguously related to the concentration of Ag nanoparticles in CS. Consequently, the transmission of Ag nanoparticles through the filter samples (MR NF BN / PA 6 and LB h-NF BN / PA 6) varied depending on their sizes, as confirmed by the excitation of two SPR peaks and intensified light scattering. Furthermore, the same figure reveals

the closest correspondence between the absorption spectra of CS of Ag nanoparticles before and after filtration through the MR NF BN / PA 6 sample. A comparative assessment of transmission capacity $T = \text{DMR}/\text{DAg}$ was conducted. Its value was found to be the highest for MR NF BN / PA 6 – $T = 98\%$ for Ag nanoparticle sizes of 56 nm, and even for the largest Ag nanoparticle sizes (around 100 nm), $T = 97\%$. In contrast, for the pure fabric, $T = 62\%$. For the LB NF h-BN / PA 6 sample, $T = 82\%$. Thus, a significant increase in the transmission coefficient of Ag nanoparticles was achieved for both PA6-based filter samples modified with boron nitride.

However, when subjected to magnetron sputtering, BN particles penetrate into the polyamide, thus creating a volumetrically modified layer, whereas the LB method forms

only a surface film, for which reason it is less effective in reducing the hydrodynamic resistance. The presented findings and their qualitative justification are consistent with the data cited in the introduction.

To assess the degree of penetration and interaction of silver ions with the polyamide structure, curves showing the concentration distribution of silver particles along the vertical axis were plotted for the PA 6 and MR NF BN / PA 6 samples (Fig. 4). The modeled computational cell of $100 \times 100 \times 100 \text{ \AA}$ was visualized before (0 ps) and after (105 ps) filtration. At the initial time point, water molecules (90 wt.%) and silver particles (10 wt.%) represented within the model as individual atoms with corresponding potentials were located above, in immediate proximity to the membrane.

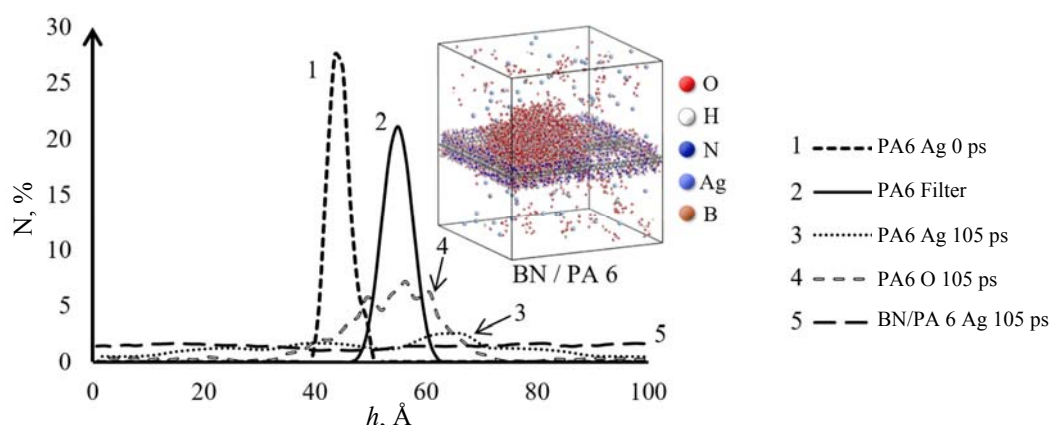


Fig. 4. Spatial distribution of atoms after their passage through the filter, according to Materials Studio 2020 data.

The filtration process involved spatial redistribution of molecules and particles. Thus, during the filtration of Ag particles through MR NF BN / PA 6, the concentration of Ag within the modeled cell became more uniform, and its gradient was minimized, which indicated the minimal interaction between BN and Ag. That is, the transmission capacity of the polyamide fabric for Ag nanoparticles increased. In the sample of pure PA 6 fabric (Fig. 4), redistribution of Ag particles was also noted, with a local increase in their concentration in the boundary regions of the filter (as can be seen in Fig. 4 – PA 6) due to van der Waals interactions. Thus, the results of molecular dynamics modeling fully confirmed the experimental data.

Conclusion

Filter samples based on polyamide fabric PA6 and modified with boron nitride nanoparticles using the Langmuir-Blodgett and magnetron sputtering methods demonstrated an increased transmission coefficient for the colloidal solution of silver nanoparticles. The introduction of boron nitride nanoparticles provided an overall improvement by reducing swelling and hydrodynamic resistance, thereby increasing the transmission capacity of the studied filter samples. This contributed to an increase in their transmission capacity, as demonstrated using the polydisperse (29, 56 and 100 nm) colloidal system of silver nanoparticles. These findings were confirmed by spectroscopic studies

consistent with the conclusions of molecular dynamics modeling that accounted for diffusion and surface effects during filtration.

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About authors

Loktionova Inna Vladimirovna, Candidate of Physical and Mathematical Sciences, Associate Professor Southwest State University (305040, Russia, Kursk, 50 Let Oktyabrya st., 94). E-mail: ms.chuhaeva@mail.ru ORCID: 0009-0005-7272-2939, SPIN code: 9474-8070, AuthorID: 738514

Abakumov Pavel Vladimirovich, Candidate of Physical and Mathematical Sciences, Associate Professor Kursk State Medical University (305041, Russia, Kursk, K. Marx st., 3). E-mail: abakumovpavel18@gmail.com ORCID: 0009-0009-1055-4019, SPIN code: 7660-5667, AuthorID: 677269

Kuzmenko Alexander Pavlovich, Doctor of Physical and Mathematical Sciences, Professor, Chief Research Scientist Southwest State University (305040, Russia, Kursk, 50 Let Oktyabrya st., 94). E-mail: apk3527@mail.ru ORCID: 0000-0001-7089-0692, SPIN code: 2312-6978, AuthorID: 41744

Kolpakov Artem Igorevich, Postgraduate Student, Southwest State University (305040, Russia, Kursk, 50 Let Oktyabrya st., 94) E-mail: artem.kolpakov.96@mail.ru ORCID: 0009-0004-8571-8544, SPIN code: 8221-5955, AuthorID: 1243978

Mamontov Vladimir Alexandrovich, Postgraduate Student Southwest State University (305040, Russia, Kursk, 50 Let Oktyabrya st., 94). E-mail: vladimir-mamontov2013@yandex.ru ORCID: 0000-0003-0592-3851, SPIN code: 1627-8010, AuthorID: 1118347

Novikov Evgeny Alexandrovich, Candidate of Physical and Mathematical Sciences, Senior Lecturer, Southwest State University (305040, Russia, Kursk, 50 Let Oktyabrya st., 94). E-mail: novikov.2403@mail.ru ORCID: 0000-0002-8824-1540, SPIN code: 7321-5660, AuthorID: 1040884

Petrova Lyudmila Pavlovna, Candidate of Physical and Mathematical Sciences, Associate Professor Southwest State University (305040, Russia, Kursk, 50 Let Oktyabrya st., 94). E-mail: galarina55555@mail.ru ORCID: 0009-0007-8883-5983, SPIN code: 7656-4073, AuthorID: 651895