

# Preparation and study of the physicochemical characteristics of multilayer polymer composites based on poly(ethyleneimine)-stabilized copper nanoparticles and poly(sodium 2-acrylamide-2-methyl-1-propanesulfonate)

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## Поли (этилениминде) тұрақтандырылған мыс нанобөлшектері және поли (2-акриламидо-2-метил-1-натрий пропансульфонаты) негізіндегі мультиқабатты полимерлік композит алу және оның физикалық-химиялық сипаттамаларын зерттеу

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## Получение и изучение физико-химических характеристик мультислойных полимерных композитов на основе стабилизированных поли(этиленимином) наночастиц меди и поли(2-акриламид-2-метил-1-пропансульфоната натрия)

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Multilayer films were synthesized from a complex of branched polyethyleneimine (PEI) with copper nanoparticles (PEI-CuNPs) and sodium poly-2-acrylamide-2-methyl-1-propanesulfonate (PAMPSNa), applied layer-by-layer (LbL) on a solid support in an acidic medium. Protonation of the amino groups of PEI in an acidic medium increases the positive charge of the PEI-CuNPs system to +43.5 mV and promotes the formation of an interpolyelectrolyte complex between the positively charged PEI-CuNPs and the highly charged anionic polyelectrolyte PAMPS, the  $\zeta$ -potential of which was -141 mV. AFM images and SEM micrographs showed a uniform distribution of spherical copper nanoparticles in the homogeneous structure of the multilayer film. The optical characteristics and hydrodynamic dimensions of PEI-CuNPs indicate the formation of PEI-CuNPs nanoparticles with sizes of 60-300 nm, with an average size of up to 100 nm. Copper nanoparticles distributed uniformly in a multilayer PEI-CuNPs/PAMPS film may be of interest for applications in the field of membrane catalysis, biochips, sensor membranes, and controlled drug delivery.

**Keywords:** polyethylenimine; sodium poly-2-acrylamide-2-methyl-1-propanesulfonate; complexes of PEI-Cu<sup>2+</sup> and PEI-CuNPs; layer-by-layer (LbL) deposition; multilayered thin films of PEI-CuNPs/PAMPS.

Қышқыл ортада қатты субстратқа layer-by-layer (LbL) әдісімен қабатпен жағылған мыснанобөлшектері (PEI-CuNPs) және поли-2-акриламид-2-метил-1-натрий пропансульфонаты (PAMPSNa) бар тармақталған полиэтиленмин (PEI) кешенінің қатысуымен мульти қабатты пленкалар синтезделді. PEI амин топтарының қышқыл ортада протондалуы PEI-CuNPs жүйесінің зарядын +43,5 mV-ге дейін арттырады және зарядталған PEI-CuNPs жоғары зарядталған анионды PAMPS полиэлектролит арасындағы интерполиэлектролит кешенінің пайда болуына ықпал етеді,  $\zeta$ -potential -141 mV-ге тең. АСМ суреттері мен микрофотографиялары көп қабатты пленканың біртекті құрылымында мыстың сфералық нанобөлшектерінің біркелкі таралуын көрсетті. PEI-CuNPs оптикалық сипаттамалары мен гидродинамикалық өлшемдері нанобөлшектерінің пайда болуын көрсетеді. Өлшемдері 60-300 нм, орташа мөлшері 100 нм дейін. PEI-CuNPs/PAMPS көп қабатты пленкасында біркелкі бөлінген мыс нанобөлшектері мембраналық катализ саласында, биочиптерді, сенсорлық мембраналарды және дәрі-дәрмектерді жеткізуді басқаруда қолдануға қызығушылық тудыруы мүмкін.

**Түйін сөздер:** полиэтиленимин; поли-2-акриламид-2-метил-1-натрий пропансульфонаты; PEI-Cu<sup>2+</sup> және PEI-CuNPs кешендері; қабатты тұндыру (LbL); көп қабатты жұқа PEI-CuNPs/PAMPS қабықшалары.

Синтезирваны мультислойные пленки с участием комплекса разветвленного полиэтиленимина (PEI) с наночастицами меди (PEI-CuNPs) и поли-2-акриламид-2-метил-1-пропансульфонатом натрия (PAMPSNa), нанесенные послойно методом layer-by-layer (LbL) на твердую подложку в кислой среде. Протонирование аминокрупп PEI в кислой среде увеличивает положительный заряд системы PEI-CuNPs до +43,5 mV и способствует образованию интерполиэлектролитного комплекса между положительно заряженным PEI-CuNPs и сильнозаряженным анионным полиэлектролитом PAMPS,  $\zeta$ -potential которого равен -141 mV. АСМ-изображения и микрофотографии СЭМ показали равномерное распределение сферических наночастиц меди в однородной структуре мультислойной пленки. Оптическая характеристика и гидродинамические размеры PEI-CuNPs указывают на образование наночастиц PEI-CuNPs с размерами 60-300 нм, со средним размером до 100 нм. Наночастицы меди, равномерно распределенные в мультислойной пленке PEI-CuNPs/PAMPS могут представлять интерес для применения в области мембранного катализа, в создании биочипов, сенсорных мембран и контролируемой доставки лекарственных препаратов.

**Ключевые слова:** полиэтиленимин; поли-2-акриламид-2-метил-1-пропансульфонат натрия; комплексы PEI-Cu<sup>2+</sup> и PEI-CuNPs; послойное осаждение (LbL); мультислойные тонкие пленки PEI-CuNPs/PAMPS.



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### 1. Introduction

One of the promising and intensively developing areas is the production of multilayer membranes and films by the layer-by-layer (LbL) method, by embedding metal nanoparticles into their matrix to give them the desired properties and functions. Such thin-layer films have found wide application in the creation of biochips, sensor membranes, membrane nanocatalysts, for the stabilization of nanoparticles and controlled delivery of drugs, etc. The successful use of polyelectrolytes forming a complex due to covalent and hydrogen bonds, electrostatic interactions, and also due to molecular recognition made it possible to obtain new materials with unique physicochemical properties, for example, controlled thickness and morphology, uniform distribution of metal nanoparticles in the volume [1-3]. The purposeful introduction of metal nanoparticles into multilayer films makes it possible to use them as membrane nanocatalysts [4-6].

In [7-10], immobilization of mono- and bimetallic nanoparticles in the bulk of multilayer films was carried out to obtain effective nanocatalysts. It was found that the individual physicochemical properties of multilayer polymer composites depend on the choice of optimal blocks for assembling LbL capsules, the manufacturing technique, and the method of immobilization of various nanoparticles in the bulk of the films [7].

Pd nanoparticles attached to magnetic ferrite nanoparticles, supported on PAA and PEI, were used for the hydrogenation of olefin alcohols [8], and multilayer systems

PAA/PVP-Au, ethyl-3-thiophene acetate/PVP-Au [9] were used for the reduction of nitrophenol [10]. The regularities of the growth of multilayers of PEI/PAA, PEI/PSS, quaternized QPEI/PAA and QPVP/PSS based on a polymer-metal complex (PMC) with copper and cobalt ions were determined, and the effect of the nature of polymers, pH of the medium, temperature, conditions of layer formation and absorption of metals on their surfaces for the formation of nanocatalysts were studied [11-13].

Of great scientific and practical interest are synthetic polyampholytes capable of existing in various conformational and phase states, depending on the change in temperature, pH of the medium, the type and concentration of low-molecular-weight salt, and the thermodynamic quality of the solvent. Depending on the nature of the acidic and basic monomers, polyampholytes are divided into: weakly charged, highly charged polyampholytes and betaines. Representatives of fully charged macromolecules, highly charged polyampholytes, consist of charged cationic and anionic monomers and have the ability to retain charges in a wide range of pH values [14,15]. The behavior of highly charged polyampholytes depends on the composition of the copolymers and the distribution of monomer units [16]. The presence of permanent charges promotes the effective binding of metal ions, dyes and surfactants.

Copolymer of sodium 2-acrylamido-2-methylpropanesulfonate (AMPSNa) is a typical representative of highly charged polyampholytes, which belongs to the less studied polymers. Recent studies show that the use of AMPSNa and ARTAC as a monomer makes it possible to synthesize

polymer matrices with unique properties [17-20]. The importance of studies of polymers based on highly charged polyampholytes, in particular AMPSNa, is evidenced by a number of studies devoted to nanocomposite materials [21-25].

Studies on the complexation of highly charged polyelectrolytes with metal ions and the preparation of multilayer catalytic films by the LbL method have not been studied sufficiently and publications are of an episodic nature. Despite the wide range of polyelectrolytes, not all potentially applicable polymers are used to obtain multilayer nanocatalysts by LbL method.

In this work, a study was carried out on the creation of multilayers of a positively charged PEI-CuNPs complex and a negatively charged PAMPS polyelectrolyte. It is assumed that copper nanoparticles immobilized in PEI-CuNPs/PAMPS multilayers can be used as a catalytic center in the oxidation of organic substrates.

## 2. Experiment

### 2.1 Materials

Branched poly(ethylenimine) (PEI) with average-weight molecular weight  $M_w \sim 25\ 000$  and number-average molecular weight  $M_n \sim 10\ 000$  was purchased from Sigma-Aldrich GmbH (Figure 1).

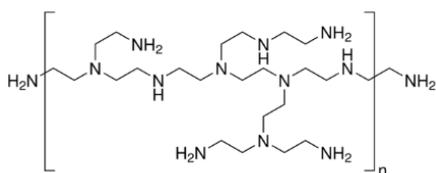


Figure 1 – Branched PEI

2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution (AMPS) (50 wt. % in aqueous solution) is the product of Sigma-Aldrich GmbH (Figure 2).

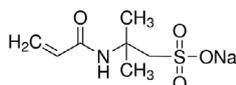


Figure 2 – AMPSNa

Copper (II) acetate monohydrate  $[Cu(CH_3COO)_2 \cdot H_2O]$  and ammonium persulfate (APS) were purchased from Sigma-Aldrich GmbH and Changzhou Qi Di Chemical Co (China) and used without further purification.

### 2.2 Methods

#### 2.2.1 Preparation of PEI-Cu<sup>2+</sup> and PEI-CuNPs complexes

PEI-Cu<sup>2+</sup> and PEI-CuNPs complexes were obtained according to the method described in [26]. When the solution of

copper (II) acetate was poured into the PEI solution slowly, with constant stirring, the solution acquired a dark blue color (Figure 3, a). This indicated the formation of a 4:1 polymer-metal complex PEI-Cu<sup>2+</sup> which means that 4 monomer units of PEI coordinate with one copper ion. When sodium borohydride interacted with PEI-Cu<sup>2+</sup>, the solution changed color from dark blue to dark brown (Figure 3b). The reduction of copper ions coordinated with PEI was accompanied by a short-term evolution of gaseous hydrogen. The resulting dark brown solution of PEI-CuNPs was dialyzed for 24 hours to remove low molecular weight impurities (Figure 3, c).

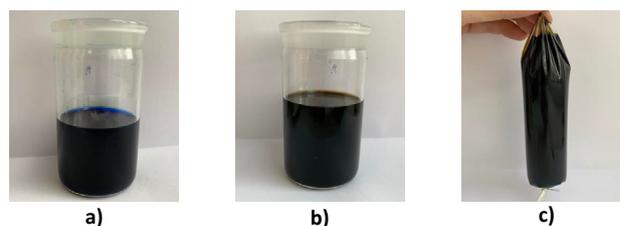
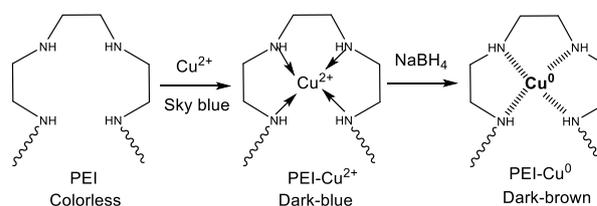


Figure 3 – PEI - Cu<sup>2+</sup> complex (a); PEI-CuNPs nanoparticles (b), dialysis of PEI-CuNPs nanoparticles (c)

The formation of four coordination complexes between the repeating units of PEI and bivalent copper ions, as well as the reduction of the PEI-Cu<sup>2+</sup> complex with sodium borohydride to the formation of Cu<sup>0</sup> nanoparticles stabilized by PEI, can be represented by the following scheme



Scheme 1 – Scheme of the formation of the PEI-Cu<sup>2+</sup> coordination complex and its reduction with sodium borohydride to the zero-valence state

#### 2.2.2 Preparation of SiO<sub>2</sub> substrate - SurfusNanoLane for the deposition of PEI-CuNPs/PAMPS multilayers

For the deposition of multilayers, a SiO<sub>2</sub>-SurfusNanoLane substrate was used, which was kept in Piranha solution (a mixture of hydrogen peroxide and sulfuric acid in a ratio of 1:4) for 24 hours to remove organic contaminants and increase the surface hydrophilicity. Then the substrate was washed with water and dried in a stream of nitrogen.

#### 2.2.3 Layer-by-layer (LbL) deposition

The LbL assembly process was performed by immersing a solid base in a dilute solution of a positively charged

polyelectrolyte to adsorb the first monolayer, then immersing it in a negatively charged polyelectrolyte to obtain a second monolayer [27-29]. The multilayer deposition was carried out using ND-DC DipCoater Nadetech (Spain) rotary spray gun (Figure 4). Multilayers were formed on the surface of the substrates using PEI-CuNPs and PAMPS solutions with a concentration of  $10^{-2}$  mol/L at pH 4. The dipping procedure was carried out in the following order: 1) PEI-CuNPs solution; 2, 3) rinsing with distilled water; 4) PAMPS solution. In this way, PEI – CuNPs/PAMPS multilayers were obtained, consisting of 50 and 100 bilayers.



**Figure 4** – Preparation of PEI–CuNPs/PAMPS multilayers using Rotary DipCoater

#### 2.2.4 Determination of the optical characteristics of PEI-CuNPs solutions

The absorption spectra of PEI-CuNPs solutions in the ultraviolet and visible regions were measured on Specord 210 plusBU spectrophotometer (Germany, 2012). The quartz cells had an optical path length of 5 and 10 mm. All measurements were carried out at 25°C and atmospheric pressure, at a wavelength of 200-800 nm. In the spectrophotometric experiment, measurements were taken into account with a relative error of no more than 3%.

#### 2.2.5 Determination of the average hydrodynamic dimensions and zeta potential of PEI-Cu<sup>2+</sup> and PEI-CuNPs solutions

The average hydrodynamic dimensions and zeta potential of PEI-Cu<sup>2+</sup> and PEI-CuNPs solutions were determined by

dynamic laser light scattering on Malvern Zetasizer Nano ZS90 instrument (Malvern Instruments Ltd., UK). In the dynamic light scattering method, measurements were taken into account with a relative error of no more than 5%.

#### 2.2.6 PAMPS identification

The identification of PAMPS obtained by the method of radical polymerization was carried out by means of IR and NMR spectroscopy. IR spectra of PAMPS were recorded on Cary 660 FTIR IR Fourier spectrophotometer (Agilent Technologies, USA) in the frequency range 400-4000 cm<sup>-1</sup>. The limit of permissible error of the wave number scale is  $\pm 0.1$  cm<sup>-1</sup>.

<sup>1</sup>H NMR spectra were recorded on Bruker BioSpinAvance III 500 MHz NMR spectrometer (500 MHz, Germany) using deuterated water as a solvent. Chemical shifts are measured relative to the residual proton signals of the deuterated solvent.

#### 2.2.7 Study of morphological, topographic and structural characteristics

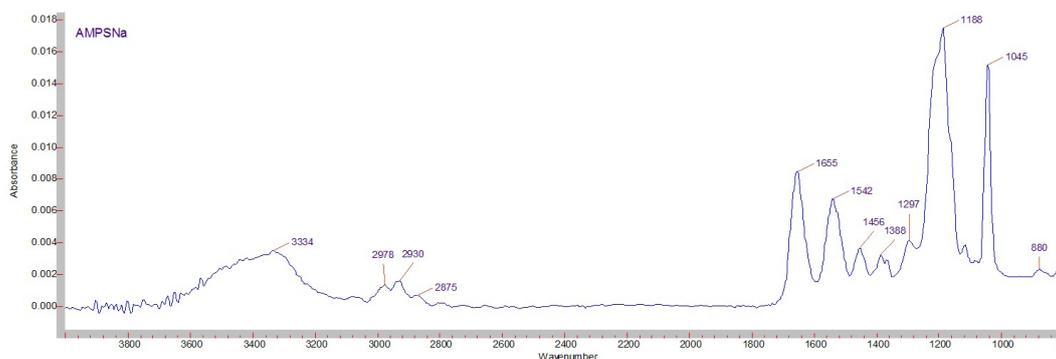
SEM JSM-6390LV scanning electron microscope (Jeol, Japan) was used to study the surface morphology of the obtained multilayers deposited on SiO<sub>2</sub>-SurfusNanoLane substrate. The measurements were carried out in a high vacuum mode using a secondary electron detector at an accelerating voltage of 15 kV. Carbon was sprayed onto the surface of the samples using magnetron sputtering of carbon fiber to increase conductivity. The samples were mounted on aluminum rods with conductive carbon tape.

The topographic characteristics of the multilayer were obtained using scanning probe microscopy SmartSPM-1000 (Russia) with a scanning range of 100x100x15 microns. Scanner resonant frequencies > 7 kHz in XY and > 15 kHz in Z.

### 3. Results and Discussion

#### 3.1 Synthesis and characterization of PAMPS

PAMPS was obtained by radical polymerization of a 30% aqueous AMPS solution in the presence of 0.25% APS at 50°C for 4 h. Unreacted monomers were removed by dialysis through a membrane in a container with distilled water with a volume of 5 L, followed by drying in an oven for 5 h, in a refrigerator for 3 h, and in a lyophilic unit for 3 h. Figure 5 shows the IR spectrum of PAMPS obtained by the method of radical polymerization.



**Figure 5** – IR absorption spectrum of PAMPS

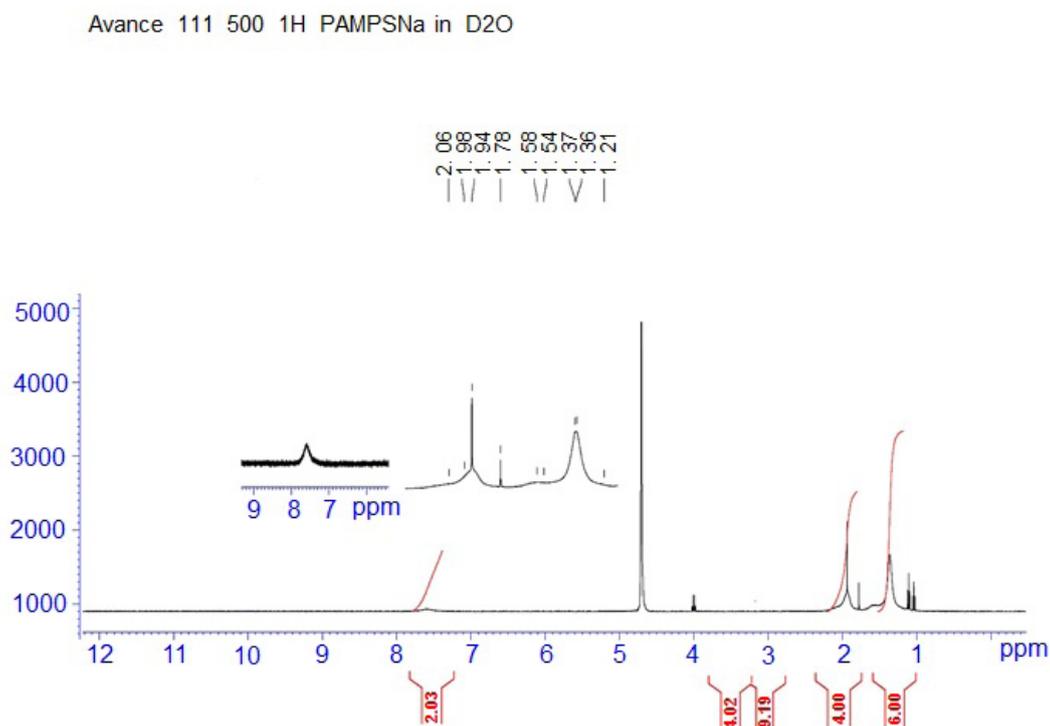


Figure 6 –  $^1\text{H}$  NMR spectra of PAMPS

The absorption spectra of PAMPS are characterized by the corresponding peaks of bending and stretching vibrations of functional groups. The broad absorption band at  $3334\text{ cm}^{-1}$  corresponds to stretching vibrations of N-H groups. Stretching vibrations of the carbonyl group of the primary amide appear at  $1655\text{ cm}^{-1}$ . Bending vibrations of C – N and C – NH amino groups appear at  $1542\text{ cm}^{-1}$ . The absorption bands at  $1388\text{ cm}^{-1}$  and  $1297\text{ cm}^{-1}$  correspond to the  $-\text{CH}_2-$  and CH groups of the polymer ridge. The characteristic S = O absorption bands appear in the regions of  $1045\text{ cm}^{-1}$  and  $1188\text{ cm}^{-1}$  [17,30,31].

The structure of PAMPS was also identified by  $^1\text{H}$  NMR spectroscopy (Figure 6). The data obtained show the presence of 6H protons of 2 methyl groups, resonating in the region of 1.36 ppm, which confirms the linear structure of PAMPS and is in good agreement with the data of [32].

### 3.2 UV-Vis absorption spectra of PEI-CuNPs before and after dialysis

Figure 7 shows the results of a study of a colloidal solution of PEI-CuNPs by UV-Vis spectroscopy before and after dialysis. According to [33], the absorption spectrum of a copper acetate solution is characterized by a maximum at a wavelength of  $\lambda = 800\text{ nm}$ . In the spectrum of the PEI solution, no maxima are observed in the wavelength range of 200-1000 nm. When a copper acetate solution is added to an aqueous PEI solution, a maximum appears in the spectrum at a wavelength of  $\lambda = 620\text{ nm}$  and a maximum characteristic of a pure copper solution disappears, which indicates the formation of PEI- $\text{Cu}^{2+}$  complex.

The formation of PEI-CuNPs nanoparticles is characterized by the appearance of an absorption band at 535-540 nm. After dialysis for 24 h, the absorption spectra of PEI-CuNPs did not undergo significant changes, and the maximum of the absorption band at 540 nm remained practically unchanged for several months. This indicates the high stability of PEI-CuNPs nanoparticles. The decrease in the spectrum intensity after dialysis is associated with the removal of small nanoparticles, as demonstrated in the next section.

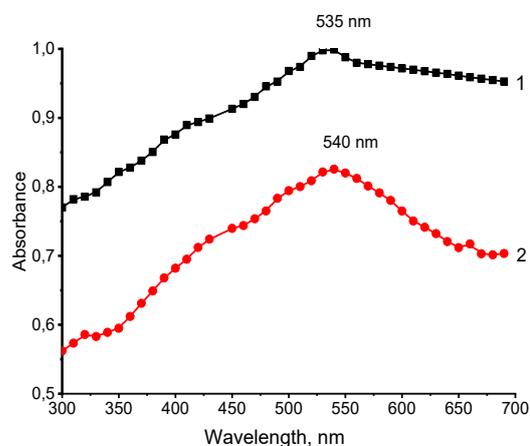


Figure 7 – UV-Vis absorption spectra of the colloidal PEI-CuNPs solution before (1) and after (2) dialysis for 24 h

### 3.3 Average hydrodynamic dimensions and zeta potential of PEI and PEI-CuNPs solutions

Figure 8 shows a histogram of the numerical size and  $\zeta$ -potential distribution of the pure PEI solution obtained by dynamic light scattering. The histogram of the hydrodynamic particle size distribution of pure PEI is mainly divided into two ranges with an average particle size of 3-200 nm and a range of size scatter of 3-4 nm and 200 nm, respectively (Figure 8, a). More than 70% of them fall within the 3-4 nm size range. The zeta potential of the pure PEI solution is positive and is  $+2.95 \pm 0.1$  mV (Figure 8, b).

The distribution of PEI-CuNPs nanoparticles before dialysis is bimodal. The average hydrodynamic sizes of nanoparticles vary from 65 to 198 nm (Figure 9, a). In this case, particles with a size of 198 nm prevail, the amount of which is 96%. The zeta potential of the PEI-CuNPs solution before dialysis is  $+32.9 \pm 1.6$  mV (Figure 9, b).

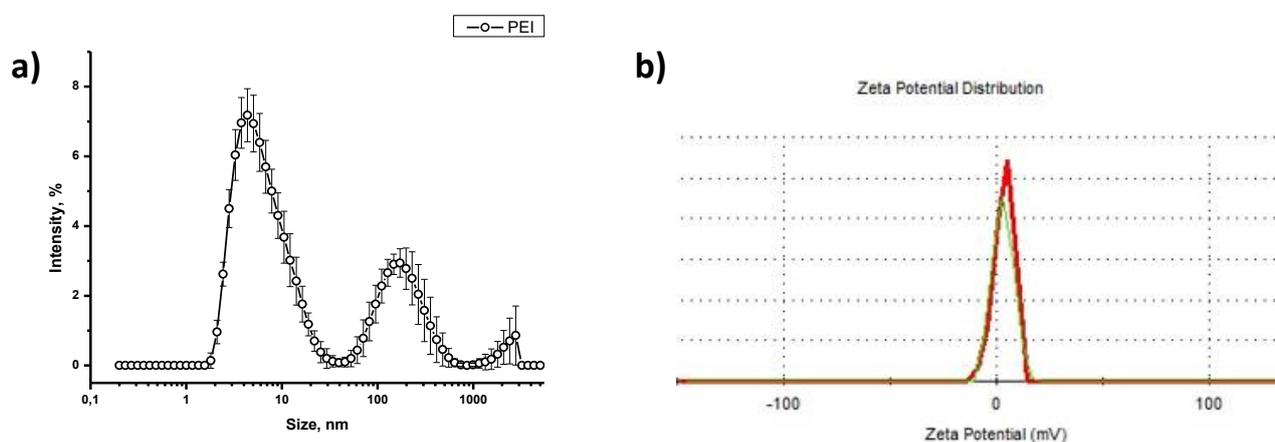


Figure 8 – Histogram of PEI distribution by hydrodynamic dimensions (a) and  $\zeta$ -potential of the solution (b)

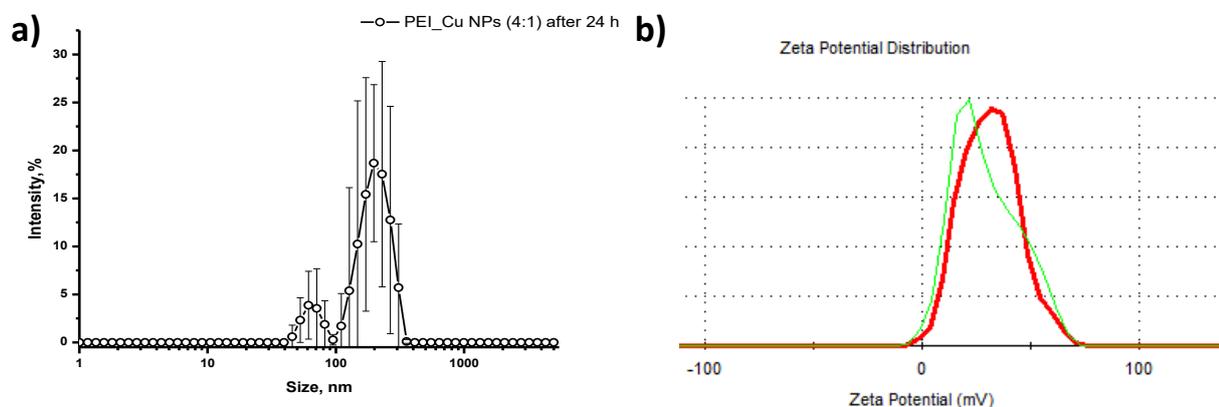
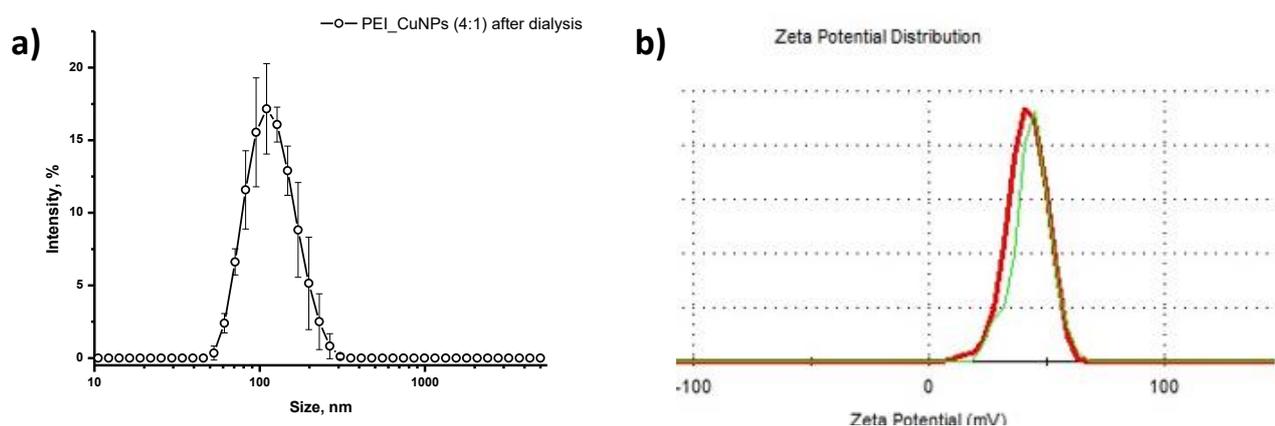


Figure 9 – Histogram of the PEI-CuNPs distribution by hydrodynamic dimensions (a) and  $\zeta$ -potential of the solution (b) before dialysis

The histogram of the hydrodynamic size distribution of PEI-CuNPs nanoparticles with an average particle size of 100 nm and a particle scatter range of 60-300 nm is shown in Figure 10, a. It can be seen that the distribution of copper nanoparticles in the PEI-CuNPs solution after dialysis became monomodal, i.e. it can be assumed that only large PEI-CuNPs nanoparticles remained in the solution, while small nanoparticles were washed out. The solution has a positive zeta potential corresponding to  $+43.5 - 2.04$  mV (Figure 10, b), since copper nanoparticles are chemisorbed with a positively charged polyelectrolyte - PEI at pH = 4.0.

This also indicates the stability of the aqueous suspension of PEI-CuNPs, which is provided due to the prevalence of electrostatic repulsion between positively charged particles reducing the possibility of aggregation. The positive charge of the PEI-CuNPs means it will form a polyionic complex with the negatively charged PAMPS.

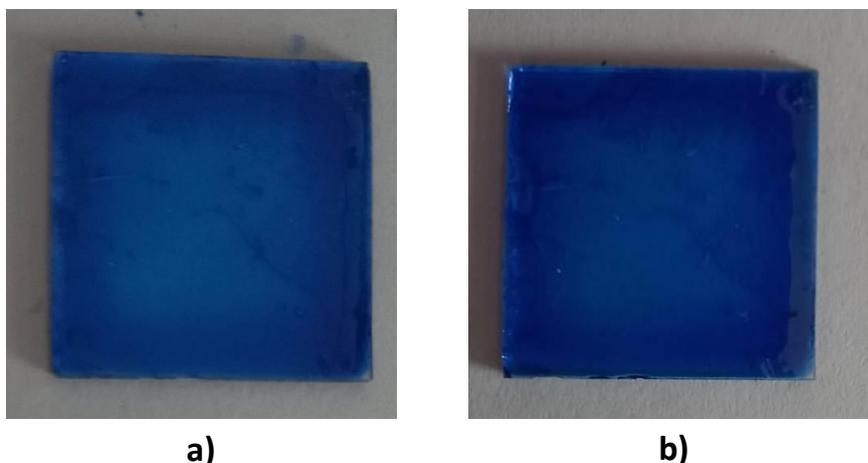


**Figure 10** – Histogram of the PEI-CuNPs distribution by hydrodynamic dimensions (a) and  $\zeta$ -potential of the solution (b) after dialysis

#### 3.4 Preparation of PEI-CuNPs/PAMPS multilayers

In order to create multilayer films by the LbL method, we used solutions of a positively charged polyelectrolyte - PEI-CuNPs and a negatively charged polyelectrolyte - sodium poly-2-acrylamide-2-methyl-1-propanesulfonate (PAMPSNa). SiO<sub>2</sub>-SurfusNanoLane was used as a substrate, on which positively

charged PEI-CuNPs nanoparticles ( $\zeta = + 43.5 \pm 2.04$  mV) and negatively charged PAMPS ( $\zeta = -141 \pm 7$  mV) were alternately deposited. As can be seen from Fig. 11, the substrate is coated uniformly with PEI-CuNPs/PAMPS multilayers, consisting of 50 (Figure 11, a) and 100 layers (Figure 11, b) painted in a saturated blue color.



**Figure 11** – Multilayers: a – PEI-CuNPs/PAMPS (50 layers); b – PEI-CuNPs/PAMPS (100 layers) applied to the plate using the layer-by-layer method

Figure 12 shows AFM images of PEI-CuNPs/PAMPSNa multilayer films (50 layers) deposited on a silicon substrate. It is seen that the surface of multilayer films is sufficiently smooth and porous. The pores are spherical. A granular morphology with a developed surface structure with a grain size of 50-130 nm is observed. The roughness of multilayer PEI-CuNPs/PAMPS films is small and averages  $\geq 20$  nm. The formation of a uniform surface of multilayers is apparently associated with the

formation of interpolyelectrolyte complexes with positively charged PEI-CuNPs nanoparticles and negatively charged PAMPS macromolecules stabilized by polyionic contacts.

The data of the atomic force microscopy are confirmed by the results of the scanning electron microscope (Figure 13). In homogeneous multilayers, evenly distributed and isolated copper nanoparticles, which have a spherical shape, can be seen.

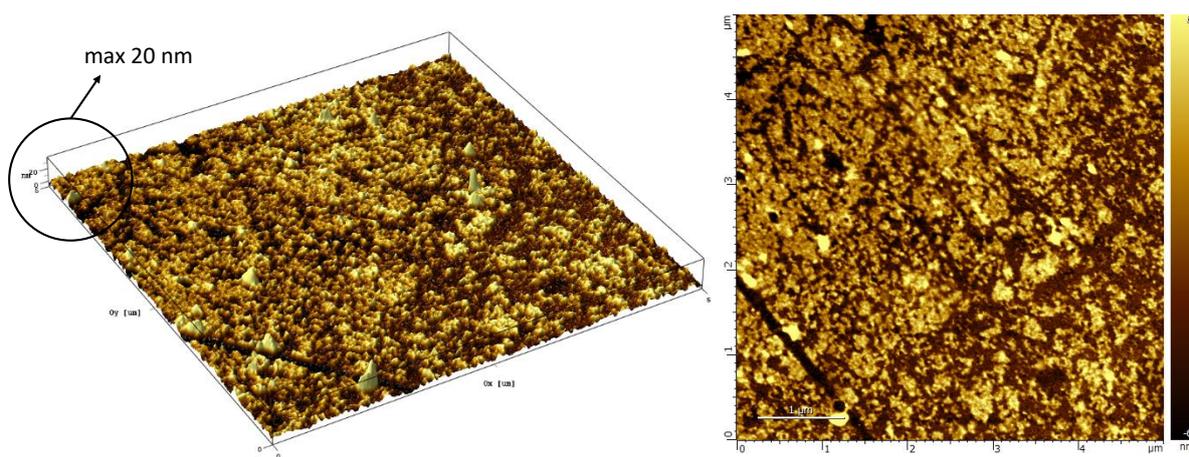


Figure 12 – Surface topography of PEI-CuNPs/PAMPS multilayer film (50 layers)

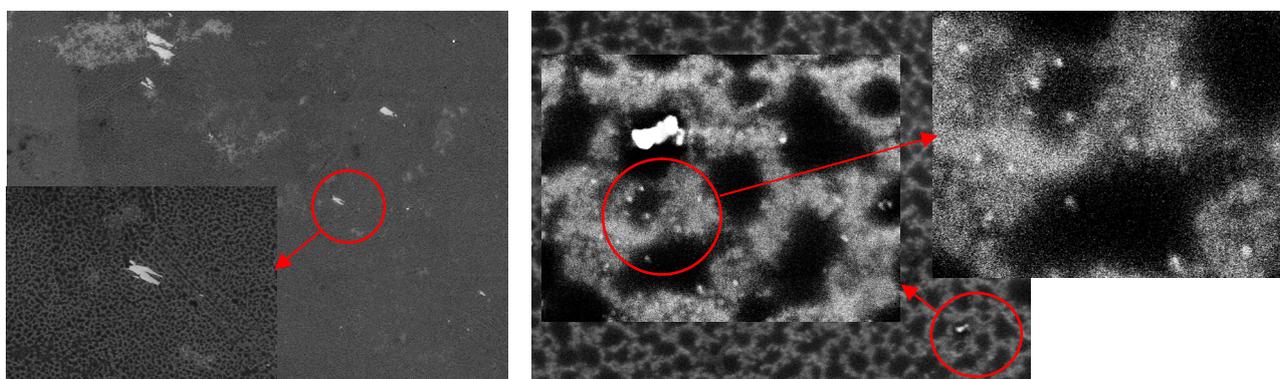


Figure 13 – SEM micrographs of PEI-CuNPs/PAMPS multilayer film

#### 4. Conclusion

Multilayered thin films composed of PEI-CuNPs/PAMPS have been obtained by layer-by-layer deposition of positively charged PEI-CuNPs and negatively charged PAMPS on the surface of  $\text{SiO}_2$ . In aqueous solution PEI, PEI- $\text{Cu}^{2+}$  and PEI-CuNPs were characterized by UV-Vis spectroscopy, DLS, and zeta-potential. In solid state multilayers of PEI-CuNPs/PAMPS were studied by AFM and SEM. It was found that nanoparticles of

copper are uniformly distributed within multilayers and in perspective can be used as membrane catalysts for oxidation of organic substrates.

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