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INFLUENCE OF NANOPARTICLES OF CuO ON THE STABILITY AND CONDUCTIVITY OF BLM

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This study aims to provide arguments for an increase in the stability of bilayer lipid membranes (BLM) in an electrical field in presence of CuO nanoparticles. Moreover, the sustainability of BLM becomes more stable with increasing of nanoparticles concentration. It is shown that an increase in the stability of BLM in an electrical field is mainly due to an increase in the coefficient of linear tension of the edge of a pore, which is forming in BLM. It is shown as well, that the presence of nanoparticles of CuO in the solution surrounding BLM leads to a decrease in the conductivity of the BLM.

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Introduction. In recent years in many areas of science and practice a tendency for more and more widespread use of nanoparticles arose. Nanoparticles have a whole range of unique properties that strongly distinguish them from the properties of macroscopic materials. Despite the impressive prospects for the use of nanoparticles, their use raises concerns because there are strong reasons to believe that in many cases they exhibit incompatibility with respect to biological object and negative consequences may occur due to their interaction with living organisms [1–3]. As in literature is shown in many cases the interaction of nanoparticles with membranes is an important and determining factor of their biological activity. A direct study of the interaction of nanoparticles with cell membranes is a quite difficult task. For this reason, it is convenient to carry out experiments on model systems such as the bilayer lipid membranes (BLM) [4–6]. Experiments on BLM have a number of advantages, in comparison with the experiments on biological membranes, since they allow one to conduct experiments under controlled conditions, and the interpretation of results are practically unambiguous. The results obtained with BLM give an opportunity to understand how nanoparticles affect the most important parameters of native membranes: stability and conductivity. Nowadays in the range of the most interesting nanoparticles are metal oxides especially the oxides of Cu, Zn and Al [7–9].

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In this paper we discuss the effect of CuO on the stability and conductivity of BLM. CuO has been widely used in practice for many years. This substance is also a good conductor of electric current, and this property is enhanced at the nanolevel, therefore, CuO nanoparticles are used in the production of semiconductors [10, 11]. Due to antimicrobial properties, CuO nanoparticles are also used in the textile industry, in paints, plastics and food containers [12, 13]. Studies have shown that copper oxide nanoparticles can penetrate the root cells of some plant species, cause severe mutagenic damage to DNA and delay the development of roots and shoots of plants. At least some food crops can be seriously affected being in contact with nanoparticles consisting CuO. It was shown that the effect of nanoparticles is selective and depends on the plant species as well as on the concentration of nanoparticles [14].

Materials and Methods. In all experiments BLM were prepared at room temperature (20–25°*C*) according to the technique described in [15]. Experiments were performed on BLM obtained from a mixture of 1,2-dipalmitoyl-*sn*-glycero-3--[phospho-l-serine] (DPPS) and 1,2-dipalmitoyl-*sn*-glycero-3-phosphoethanolamine (DPPC) (1 : 1; 4%), which were dissolved in *n*-decane. Lipids were purchased from "Avanti Polar Lipids". BLM were produced in a 0.1 *M* NaCl solution. The diameter of the hole on which BLM was formed was 1 *mm*. Taking into account the torus on the border of the hole, the area of the planar part of the BLM was 0.65 mm^2. Nanoparticles were dissolved to a final concentration of 1 mg/mL in 0.1 *M* citric acid and 0.1 *M* sodium citrate with pH 3.8 and sonicated for 30 *min*. For measurements of the electrical parameters of the BLM, a current amplifier Keithley 427 was used according to the procedure described in [16]. A voltage was applied to the BLM by means of chlorine-silver electrodes connected to the ADC (E14-140-M) and controlled by a computer in the range of 0.2–0.6 *V*. The geometrical parameters of BLM were checked by measuring their electrical capacity by means of their cyclic current-voltage characteristics (CVC) implemented in a custom-made Lab VIEW program. The electrical capacity of the BLM was measured by applying a symmetrical triangular voltage with a sweep rate of 0.07 V/s. The measurements allowed estimating the thickness of BLM, which was 45–55 Å for all experiments. The effect of CuO nanoparticles with an average size of 20 *nm* on the stability and conductivity of BLM was studied at concentrations of 5, 20 and 50 $\mu g/mL$ of CuO. Nanoparticles are kindly provided by the Institute of Medical Physics and Biophysics of the University of Leipzig, Germany.

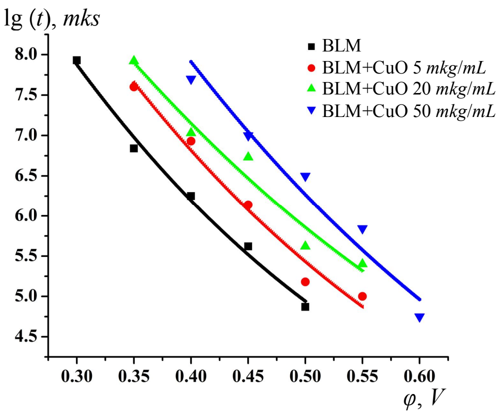
Results and Discussion. The stability of BLM in an electric field in the presence of CuO nanoparticles in a surrounding BLM solution was investigated. A main parameter characterizing the degree of stability of BLM is their mean lifetime at a given voltage across the BLM. Investigation of the stability of BLM in an electric field was carried out according to the standard procedure using the dependence of the average lifetime $\bar{t}$ of BLM on the potential φ in the form $\bar{t}(\varphi)$ [17–19]:

$$\bar{t}(\varphi) = \frac{(k_B T)^{3/2}}{4\pi D c_0 S \gamma (\sigma + C\varphi^2/2)^{1/2}} \cdot \exp\left(\frac{\pi\gamma^2}{(\sigma + C\varphi^2/2)\, k_B T}\right), \qquad (1)$$

where σ is the surface tension of the BLM; γ is the linear tension along the pore edge in the BLM; D is the diffusion coefficient of defects in the space of radii; φ is the voltage on the membrane; k_B is the Boltzmann constant; T is the temperature; C is the reduced electrical capacitance defined by the relation $C = C_0(\varepsilon_w/\varepsilon_m - 1)$, where $C_0 = \varepsilon_0\varepsilon_m/h$ is the specific electrical capacity of the BLM; $\varepsilon_w, \varepsilon_m$ and ε_0 are the dielectric constants of water, BLM and the vacuum respectively; c_0 is the concentration of pores in the BLM and S is the BLM area.

For comparison of the theoretical curve (1) with the experimental data it is convenient to introduce it in a logarithmic form:

$$\begin{gathered} \lg \bar{t} = A - \frac{1}{2}\lg(1 + M\varphi^2) + \frac{B}{1 + M\varphi^2}, \\ A = \lg\left(\frac{(k_B T)^{3/2}}{4\pi D c_0 S \gamma \sigma^{1/2}}\right), \; B = \frac{\pi\gamma^2 \lg e}{\sigma k_B T}, \; M = \frac{C}{2\sigma}. \end{gathered} \tag{2}$$



Decrease in the mean lifetime of BLM with increasing voltage in the presence of nanoparticles CuO with concentrations of:
● 5; ▲ 20; ▼ 50 (*mkg/mL*)
points are experimental data (average of five measurements at each potential difference);
solid lines are theoretical curves obtained by the least-square fitting to Eq. (2).

At first, we studied the variation of the mean lifetime of BLMs at increasing levels of voltage in the absence of nanoparticles, and then in the presence of nanoparticles. Figure presents the results of our study of the influence of the concentration of CuO nanoparticles on the stability of BLM in an electrical field.

By fitting parameters of the theoretical curves to the experimental data, in Figure the values of parameters A, B and M in Eq. (2) were determined and, hence, the values of the main parameters of BLM such as surface tension (σ), linear tension of the pore edge in the BLM (γ) and parameter c_0SD, on which the BLM stability mainly depends. The parameter c_0SD, which is the product of the number of pores c_0S on the BLM and the diffusion coefficient D of the defects in the space of radii, shows the defectiveness of the BLM, on the one hand, and the extent of diffusion growth of the pore, on the other hand.

First, the tension of BLM was determined in the absence of nanoparticles, i.e. $\sigma = 7.9 \cdot 10^{-3}\ N/m$. Using the value of σ, we can easily obtain the linear tension of the pore edge in the BLM in the absence of nanoparticles, i.e. $\gamma = 1.6 \cdot 10^{-11}\ N$. This quantity is in good agreement with the literature data [17,20]. The values of the parameters σ, γ and c_0SD determined from the experiment at different concentrations of CuO nanoparticles are given in Tab. 1.

Table 1

The parameters σ, γ and c_0SD, determined from fitting of the theoretical curve in Eq. (2) to the experimental data presented in Figure

CuO, mkg/mL	σ, N/m	γ, N	c_0SD, m^2/c
0	0.0079	$1.65\cdot10^{-11}$	$5.35\cdot10^{-22}$
5	0.0097	$1.89\cdot10^{-11}$	$1.01\cdot10^{-21}$
20	0.0124	$2.04\cdot10^{-11}$	$6.11\cdot10^{-22}$
50	0.0130	$2.37\cdot10^{-11}$	$7.64\cdot10^{-21}$

The experimental data in Figure show, that the mean lifetime of the BLM increases in the presence of CuO nanoparticles with increasing concentration. Analysis of the Eq. (1) shows, that the mean lifetime of the BLM depends more strongly on the parameter γ, the increase of which leads to an increase of the mean lifetime of BLM. This dependence is shown in Tab. 1 (the second column).

Studies were carried out to determine the effect of nanoparticles on the conductivity of BLM, the current-voltage characteristics of BLM were obtained in the presence and absence of nanoparticles in solution. It is shown that the presence of CuO nanoparticles in the electrolyte solution leads to an insignificant decrease in the conductivity of BLM with CuO concentrations of 5 and 20 mkg/mL. A pronounced decrease in the conductivity compared to the control is observed at a concentration of 50 mkg/mL (see Tab. 2).

Table 2

Conductivity of BLM in the presence of CuO nanoparticles in solution

	g, 10^{-9} Om^{-1}			
BLM + CuO	BLM in NaCl	BLM + 5 mkg/mL CuO	BLM + 20 mkg/mL CuO	BLM + 50 mkg/mL CuO
Average	0.27	0.26	0.26	0.25
Std. Error	0.01	0.01	0.01	0.01

Thus, the analysis of the obtained results shows that the presence of nanoparticles of copper oxides in the surrounding BLM solution leads to an increase in the stability of BLM in an electrical field. It is shown that an increase in the stability of BLM in an electrical field is mainly due to an increase in the coefficient of linear tension of the edge of the pore, which is formed in BLM. It is shown as well that the presence of nanoparticles of copper oxides in the surrounding BLM solution leads to a decrease in the conductivity of BLM.

Since the CuO nanoparticles used in the aqueous solution are positively charged [21,22], and there are negatively charged groups on the surface of the BLM, it can be assumed that the mechanism of action of nanoparticles on the stability and conductivity of BLM is analogous to the mechanism of action of positively charged multivalent ions (for example, calcium [23, 24]), i.e. an increase in stability and a decrease in the conductivity of BLM is associated with the compacting of the structure of BLM as a result of the adsorption of nanoparticles onto the surface of BLM.

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