

Motivation and Research Objectives

In that work reports on the investigation of the optical properties of nanocomposites consisting of Ag NPs and methylene blue Dye (MB). The actuality of research on such nanosystems is :

- the possibility of creating generalized conception about the physical interaction between the components of heterocomposite;
- the development of new nanomaterials with a wide range of applications.

Silver nanoparticles and methylene blue dye each have unique physicochemical properties [1,2]. They have practical applications in electronics, optics, sensorics, medicine and photocatalysis.

Goal

- Investigation of the optimal conditions for the synthesis of AgNPs, which exhibit intense plasmon absorption.
- Establishment of the mechanism of interaction between AgNPs and methylene blue Dye (MB). Possible practical application of the investigated nanostructures.

The method of synthesis Ag NPs

Silver nanoparticles were synthesized by the method of chemical reduction of silver ions from a solution of silver salt (AgNO_3) by a reducing agent — sodium citrate, tannin. The intensity of the LSPR band depends on the type of reducing agent (Fig. 1) and on the synthesis time (Fig. 2). In the absorption spectrum of the obtained silver nanoparticles, an intense LSPR band is recorded, the maximum of which is localized in the wavelength range of 415 ± 420 nm (reducing agent — sodium citrate).

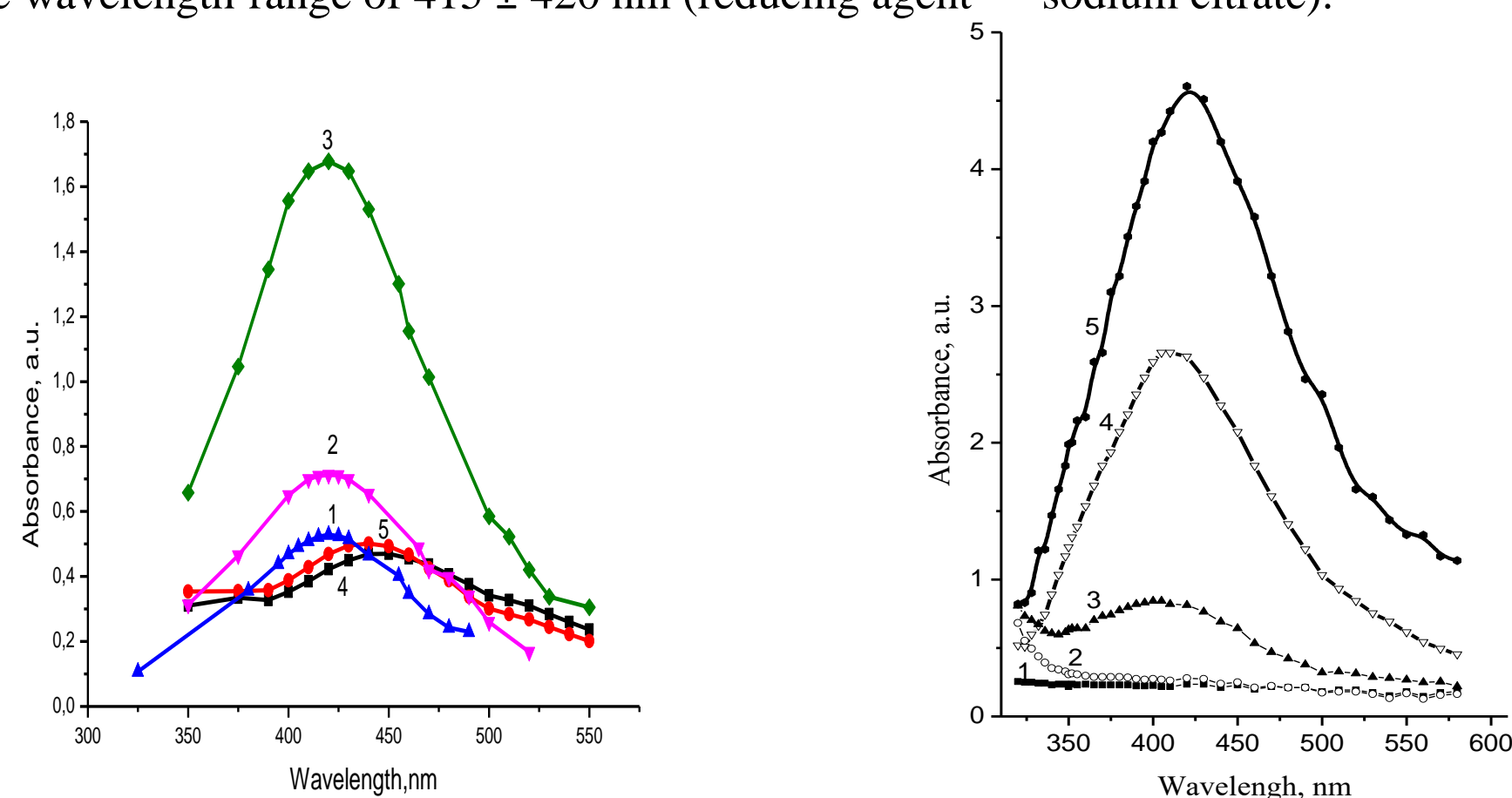


Fig. 1. Absorption spectrum of Ag NPs grown in a solution of sodium citrate (1,2,3) and tannin (4,5). Concentration of AgNO_3 , M: 2×10^{-4} (1), 2×10^{-4} (2,4), 2×10^{-4} (3,5).

Fig. 2. Dependence of the absorption spectra of silver NPs on the synthesis time, min: 10 (1); 15 (2); 20 (3); 30 (4); 40 (5). Concentrations AgNO_3 and sodium citrate = 10^{-3} M.

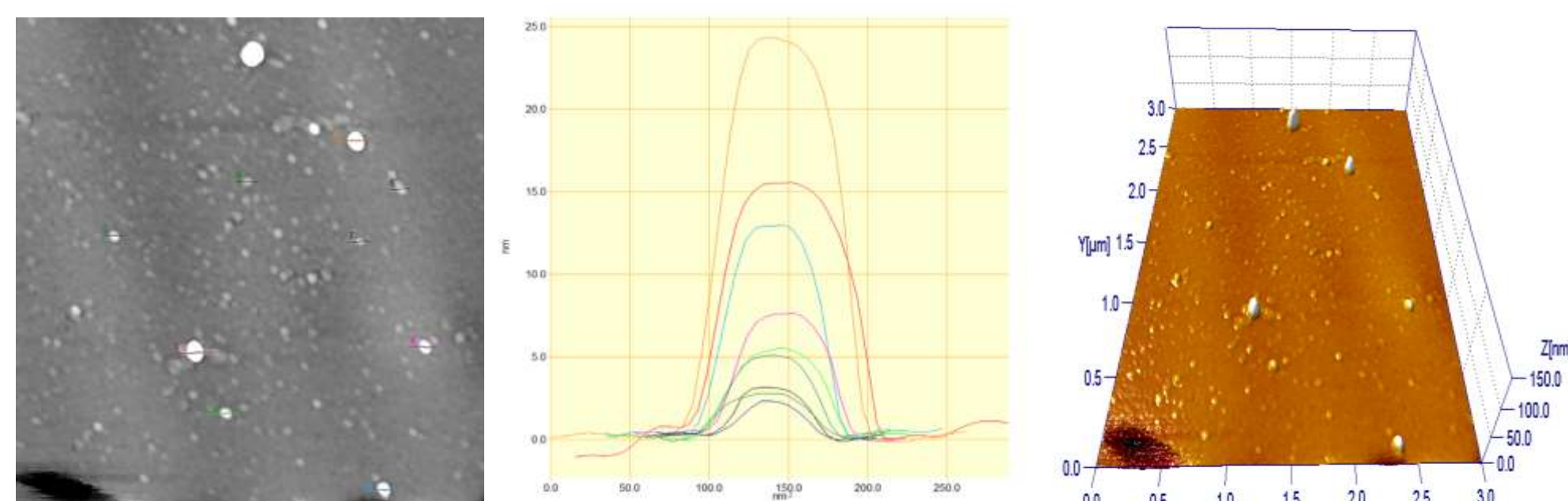


Fig. 3. The fragment of the surface NPs, the profiles of the heights NPs and 3D AFM image of the sample surface fragment

Results and discussion

From the analysis of the absorption spectra of silver sols, a number of parameters of silver particles were calculated within the framework of the Mi theory and plasma resonance absorption. The following linear dependence for the absorption coefficient has the form:

$$\frac{1}{K} = \frac{\theta_2}{\theta_1} + \frac{1}{\theta_1} \left(\frac{\lambda_{\max}^2}{\lambda} - \lambda \right)^2$$

where λ_{\max} is the wavelength at the maximum of the plasma resonance absorption, θ_1 and θ_2 are the coefficients of the linear dependence.

The values of θ_1 and θ_2 are related to the effective concentration of conduction electrons N_e , the attenuation coefficient of plasmon oscillations γ and the volume NV occupied by metal particles per unit volume, the ratios:

$$N_e = \frac{\pi m_e c^2 (\epsilon_0 + 2n^2)}{e^2 \lambda_{\max}^2}, \quad \gamma = \frac{2\pi c \theta_2^{1/2}}{\lambda_{\max}}, \quad NV = \frac{N_e e^2 \theta_1}{9\pi n^3 m_e c \gamma}$$

Table 1 shows the calculation results of these parameters for Ag NPs without dye and with Dye MB

| Dye MB | C (), M | $N_e \cdot 10^{22}, \text{cm}^{-3}$ | $\gamma \cdot 10^{15}, \text{c}^{-1}$ | $NV \cdot 10^{-7}$ | $M \cdot 10^{-6}$ |
|----------------------|--------------------|-------------------------------------|---------------------------------------|--------------------|-------------------|
| - | 2×10^{-4} | 5,742 | 5,333 | 0,314 | 0,329 |
| 1×10^{-5} M | 2×10^{-4} | 5,603 | 3,382 | 0,77 | 0,81 |
| 1×10^{-3} M | 2×10^{-4} | 5,603 | 4,113 | 0,972 | 1,02 |

The spectrum of a composite of Ag NPs with MB dye contained two bands related to the absorption of Ag NPs with $\lambda_{\max} = 420$ nm and to the absorption of a dye with $\lambda_{\max} = 630$ nm.)Fig.4.

The spectrum of a composite of Ag NPs with MB dye contained two bands related to the absorption of Ag NPs with $\lambda_{\max} = 420$ nm and to the absorption of a dye with $\lambda_{\max} = 630$ nm. It was found that with an increase in the dye concentration, the intensity of the band with $\lambda_{\max} = 630$ nm decreases, and the intensity of the SPR band of Ag P NP increases.

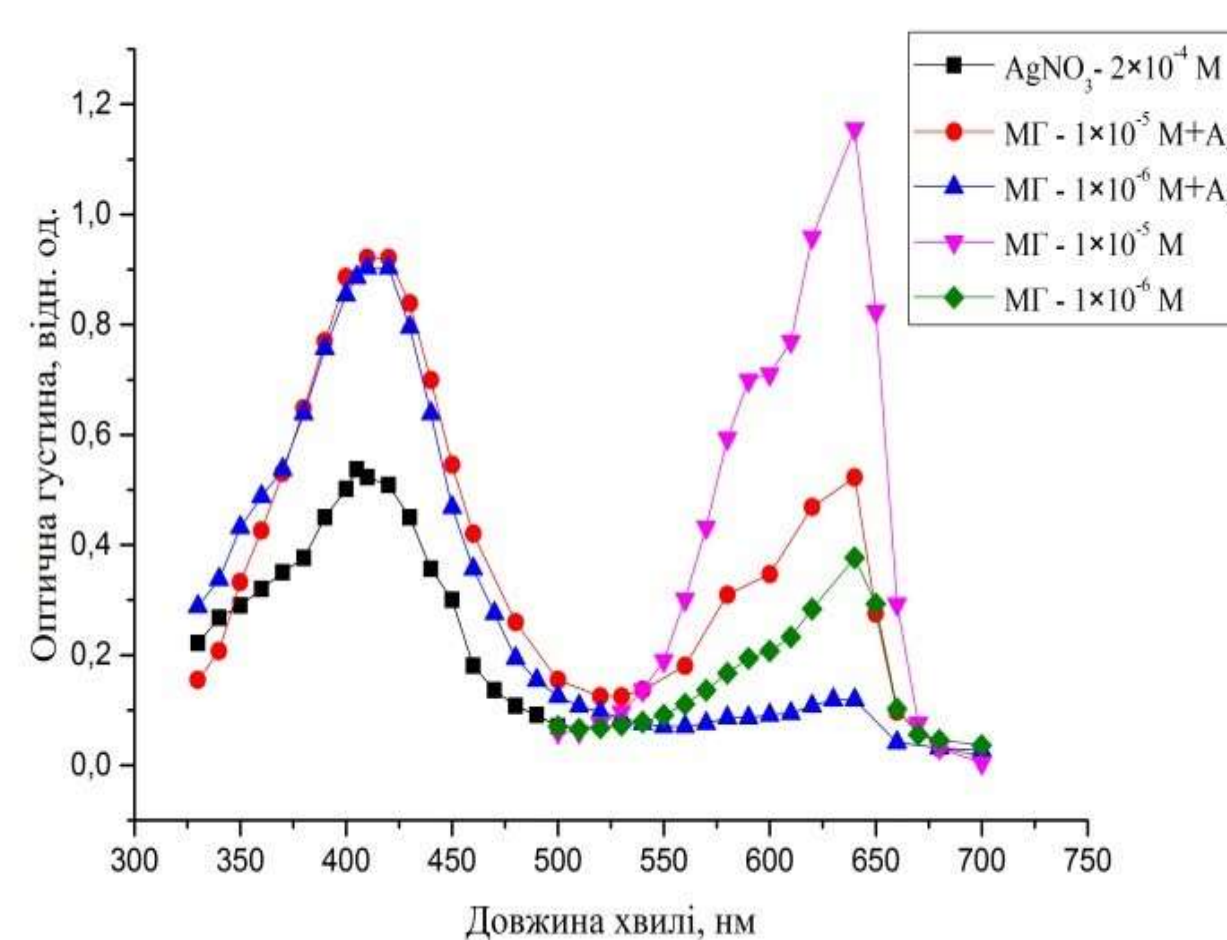


Fig.4.

Data analysis on changes in the calculated parameters of Ag NPs as a result of interaction with the dye, it can be assumed that the dye is adsorbed on nanoparticles. Indeed, this is evidenced by an increase in the volume occupied by metal particles (NV) and an increase in the mass of nanoparticles (M). It is known [3] that the damping coefficient of plasmon oscillations (γ) decreases with increasing radius of the NP, which is also observed in this case.

Conclusions

It was shown that in the composite of silver NPs with the MG dye, the dye is discolored, which is explained by its adsorption on nanoparticles with its subsequent decomposition.

The dye can decompose on the surface of AgNP due to the presence of hot electrons on the surface, created by the intraband transition of electrons (5sp) in AgNP due to LSPR.

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2. Tardivo J., Giglio A., Oliveira C., Gabrielli D., Junqueira H., Tada D., Severino D., Turchiello R., Baptista M., Methylene blue in photodynamic therapy: From basic mechanisms to clinical applications, Photodiagnosis and Photodynamic Therapy. 2(3), 175-191 (2005). doi: 10.1016/S1572-1000(05)00097-9.
3. Podlegaeva L.N., Russakov D.M., Sozinov S.A., Morozova T.V., Shvaiko I.L., Zvidentsova N.S., Kolesnikov L.V. Properties of silver nanoparticles obtained by reduction from solutions and thermal spraying in vacuum. // Polzunovskiy messenger. - 2009. - No. 3. - P. 376-380.