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EFFECT OF SODIUM CITRATE CONCENTRATION ON SERS ACTIVITY OF SILVER NANOPARTICLES PRODUCED BY TURKEVICH METHOD

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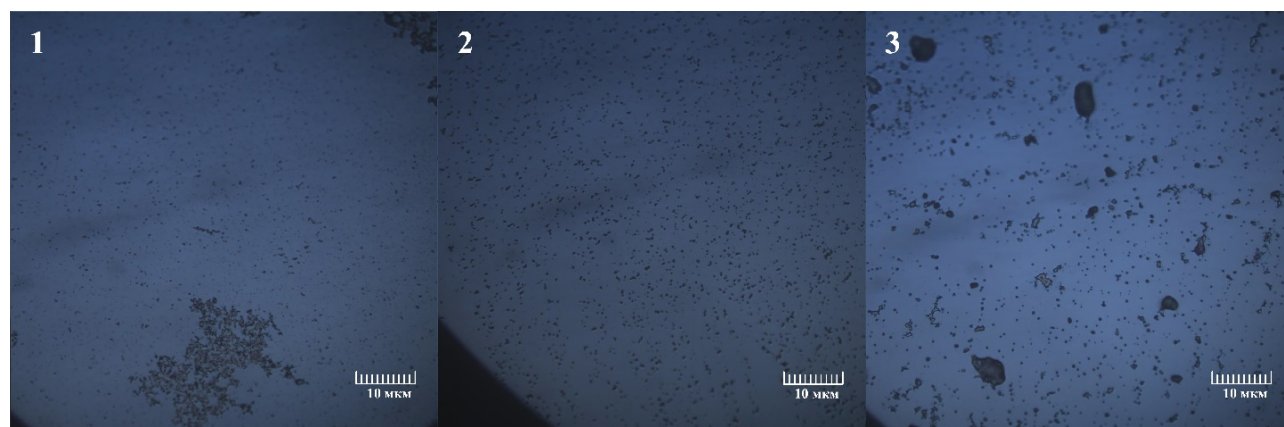
Annotation. The influence of sodium citrate concentration on detecting ability of silver nanoparticles was studied by Raman spectroscopy. Optimal parameters for achieving the maximum intensity of detection of rhodamine R6G analyte are obtained, and features of changes in size of nanoparticles and their absorbing ability are described.

Keywords: nanoparticle synthesis, citrate method, Raman spectroscopy, rhodamine R6G.

Introduction. Among various chemical approaches for obtaining metal nanoparticles, one of the widely used is the citrate method (or the Turkevich method), which makes it possible to obtain nanostructures with sizes ranging from 60 to 200 nm [1]. The main advantages of this method are its simplicity, as well as presence in the solution of one reagent (citrate anions), which simultaneously acts as a reducing agent and stabilizer. Silver nanoparticles formed by this method can, for example, be used in surface-enhanced Raman scattering (SERS) spectroscopy for detecting various types of molecules at low concentrations [2, 3].

In this work, the study of the SERS activity of obtained silver nanoparticles was carried out by recording the Raman spectra of rhodamine R6G (analyte) molecules adsorbed on their surface from a solution with a concentration of 10^{-5} M. Silver nanoparticles kept in an analyte solution were placed on a silicon substrate and dried, after that the sample was tested. For comparison, spectra of rhodamine were also obtained on silver nanoparticles without a citrate shell. Analysis was performed using a 3D scanning laser Raman confocal microscope with a spectrophotometer Confotec NR500.

Main part. The synthesis of nanoparticles was carried out at a temperature of about 100 °C for 15 minutes by adding silver nitrate (AgNO_3) and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) to boiling water. Concentration of sodium citrate varied from 0.1 to 50 mM. For samples with citrate concentrations of 0.5, 5, and 50 mM, transmission and absorption spectra were obtained. Figure 1 and 2 shows photographs of samples of silver nanoparticles obtained at various concentrations of sodium citrate.



1 – for 0.5 mM, 2 – for 5 mM, 3 – for 50 mM

Figure 1 – Images of samples from silver nanoparticles obtained using different concentrations of sodium citrate

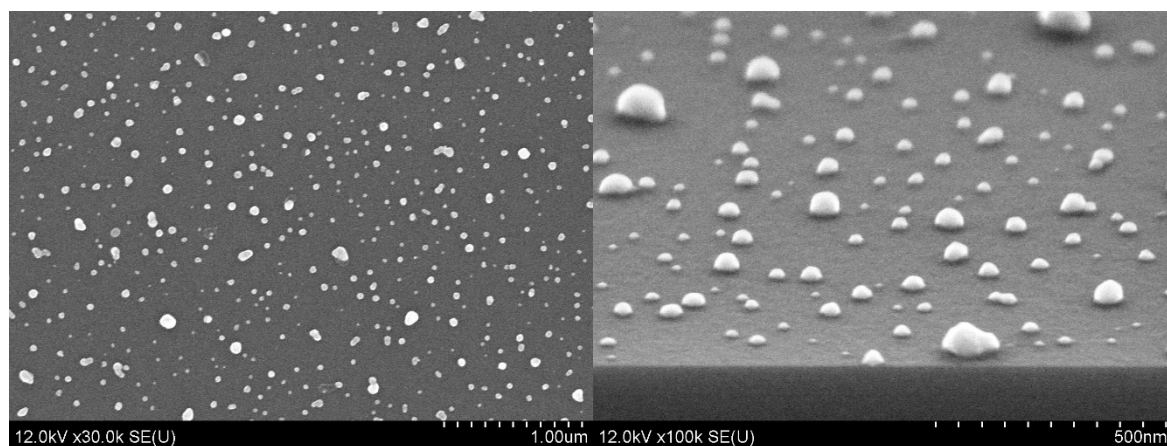
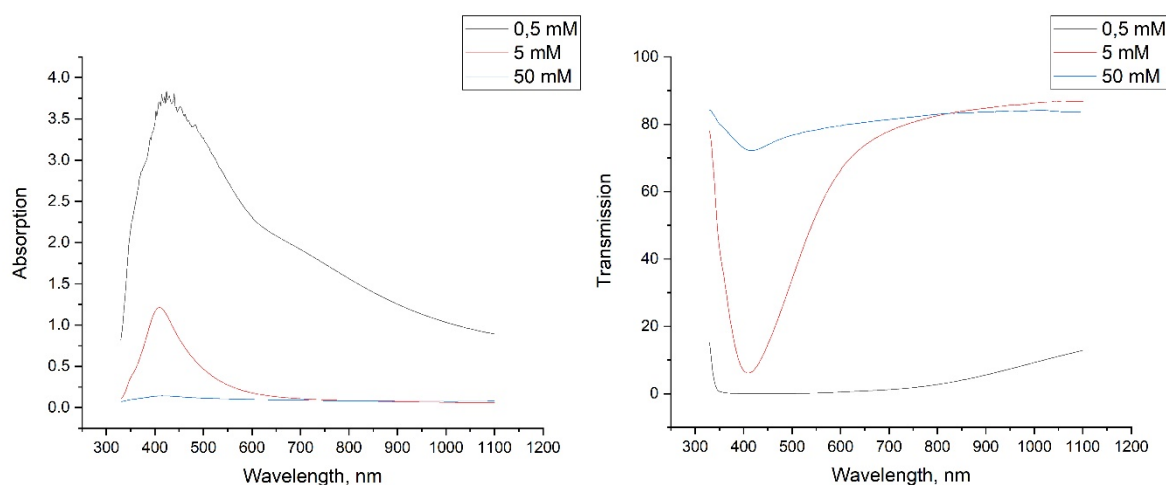


Figure 2 – SEM images of silver nanoparticles at a sodium citrate concentration of 5 mM

Based on analysis of optical and SEM images (Figure 2) obtained for these concentrations, it was found that the size distribution has 3 main modes: the first one, prevailing in all cases, with a diameter of 65 nm, and 2 others, which are different for each case. For 0.5 mM, diameters are 80 and 120 nm, for 5 mM, diameters are 120 and 170 nm, and for 50 mM – 220 and 380 nm, which indicates coalescence of nanoparticles.

Figure 3 shows absorption and transmission spectra of samples from silver nanoparticles obtained at the indicated concentrations of sodium citrate. It can be seen that an increase in the citrate concentration leads to a significant decrease in intensity of the absorption band of silver nanoparticles, and at 50 mM it is almost completely absent, which may be due to the formation of a core-shell structure, where citrate anions serve as the shell.

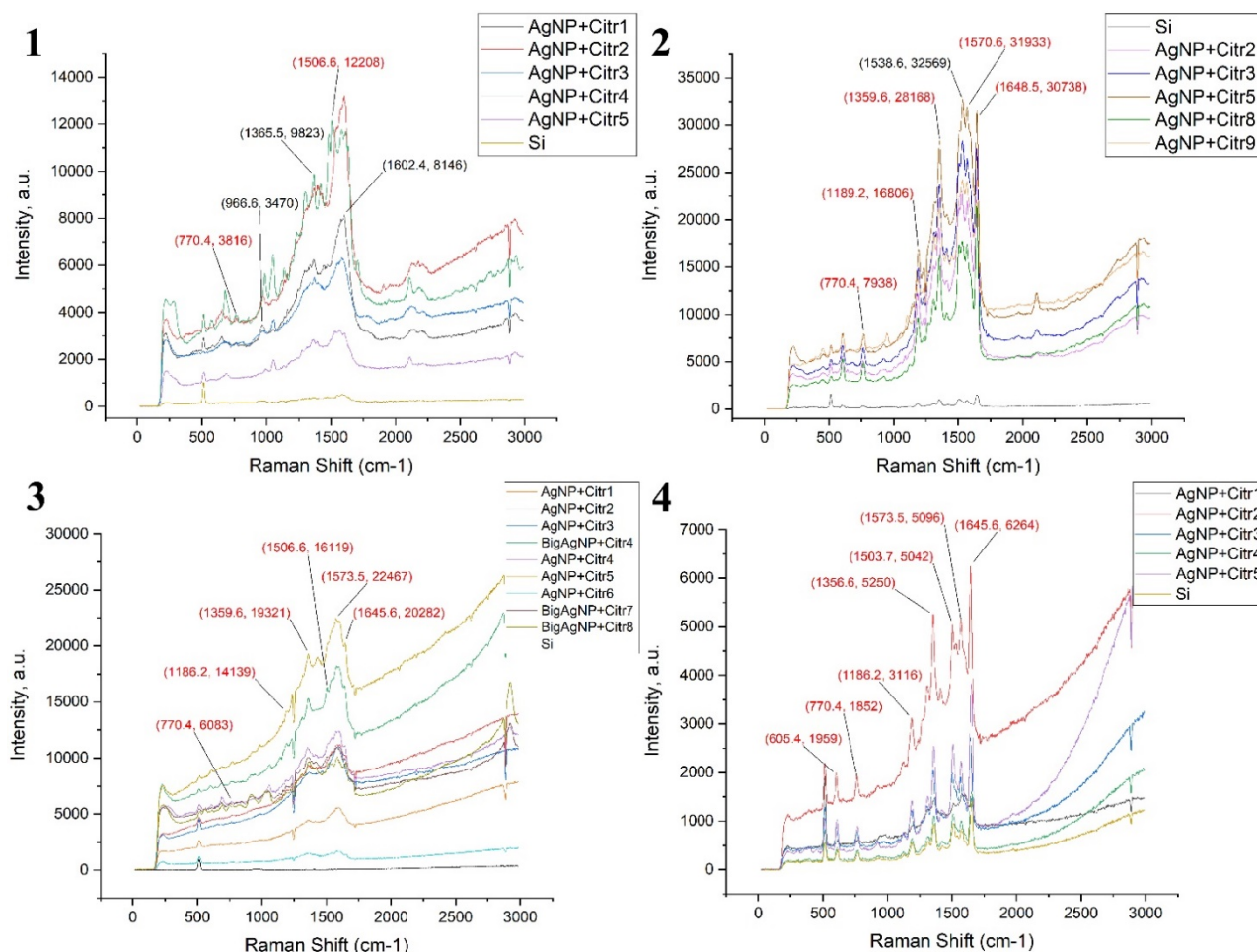


On the left – absorption spectrum, on the right – transmission spectrum

Figure 3 – Absorption and transmission spectra of silver nanoparticles obtained at different concentrations of sodium citrate (black – 0.5 mM, red – 5 mM, blue – 50 mM)

After that, Raman spectra of the analyte rhodamine R6G (10⁻⁵ M) were obtained to determine the effect of sodium citrate concentration on the SERS activity of silver nanoparticles. Spectra of rhodamine depending on citrate concentrations are shown in Figure 4 (major bands of rhodamine R6G highlighted in red).

It should be noted that at concentrations of sodium citrate less than 0.5 mM, rhodamine is difficult to detect or it is not visible at all, while in the absence of citrate anions, rhodamine is easily read, but intensity drops significantly. This behaviour may be explained due to local heating in region around the particle coated with citrate anions, which led to increase in intensity due to rise in temperature [4], as well as to the combustion of organic compounds, including citrate anions, as evidenced by the presence of intense bands at 1540 and 1600 cm⁻¹ (so-called G-bands of amorphous carbon [5]).



1 – for 0.5 mM, 2 – for 5 mM, 3 – for 50 mM, 4 – without citrate

Figure 4 – Raman spectra of R6G molecules (10^{-5} M) adsorbed on silver nanoparticles prepared by the Turkevich method using different concentrations of sodium citrate

Conclusion. It was found that with an increase in concentration of sodium citrate to 5 mM, intensity of the main peaks of rhodamine increases, after which it decreases and, simultaneously, photoluminescence background in the near-IR range begins to grow, which is associated with an increase in the concentration of citrate anions. In comparison with the sample without citrate, its intensity of the spectrum of rhodamine for most nanoparticles is in the range of 5-10 thousand a.e., while in presence of sodium citrate, intensity varies in the range of 5-30 thousand a.e. In this case, maximum is reached at concentrations of order of 1–5 mM.

References

1. Krutikov, Y. A., Kudrinsky A.A., Olenin A.Y., Lisichkin G.V. *Synthesis and properties of silver nanoparticles: achievements and prospects (in Russian)* / Y. A. Krutikov, A. A. Kudrinsky, A. Y. Olenin, G. V. Lisichkin // *Advances in Chemistry*. – 2008. – Volume 77. – Pp. 242-270.
2. Zeiri, L., Rechav, K., Porat, Z., & Zeiri, Y. *Silver Nanoparticles Deposited on Porous Silicon as a Surface-Enhanced Raman Scattering (SERS) Active Substrate* / L. Zeiri, K. Rechav, Z. Porat, Y. Zeiri // *Applied Spectroscopy*. – 2012. – Vol. 66(3). – Pp. 294–299.
3. Li, W., Guo, Y., & Zhang, P. *SERS-Active Silver Nanoparticles Prepared by a Simple and Green Method* / W. Li, Y. Guo, P. Zhang // *The Journal of Physical Chemistry C*. – 2010. – Vol. 114(14). – P. 6413–6417.
4. Zobeiri, H., Xu, S., Yue, Y., Zhang, Q., Xie, Y., & Wang, X. *Effect of temperature on Raman intensity of nm-thick WS₂: Combined effects of resonance Raman, optical properties, and interface optical interference* / H. Zobeiri, S. Xu, Y. Yue, Q. Zhang, Y. Xie, X. Wang // *Nanoscale*. – 2020. – Vol. 12(10). – P. 6064–6078.
5. Dychalska, A., Popielarski, P., Franków, W., Fabisiak, K., Paprocki, K., & Szybowicz, M. *Study of CVD diamond layers with amorphous carbon admixture by Raman scattering spectroscopy* / A. Dychalska, P. Popielarski, W. Franków, K. Fabisiak, K. Paprocki, M. Szybowicz // *Materials Science*. – 2015. – Vol. 33(4). – P. 799–805.