Synthesis of thin films from silver nanoparticles and their application as a basis for modern sensors

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Introduction

Project objective:

Creating thin films from silver nanoparticles and testing them as sensor elements. The films are formed by self-assembly at the interface between two liquids of different densities and placed on a solid substrate. They will then serve as the basis for creating sensor elements.

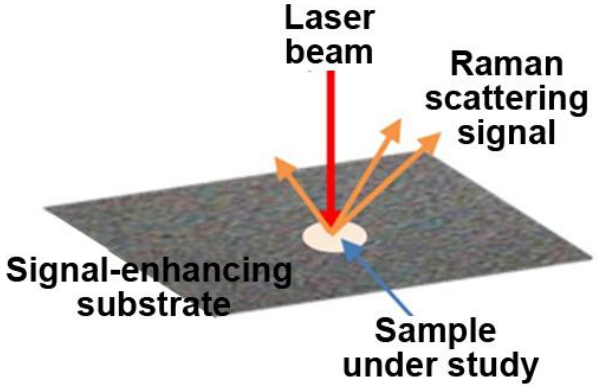
Steps to reach the project goal:

1. Study of scientific research related to the project topic (Raman spectroscopy, synthesis of nanoparticles (AgNPs), production of solid substrates for spectrometry) and literature on the project topic.
2. Synthesis of silver nanoparticles and study of the resulting solutions.
3. Self-assembly of silver nanoparticles at the phase boundary and study of its characteristics.
4. Transferring the obtained thin films of silver nanoparticles onto a solid substrate.
5. Studying the microstructure of films with silver nanoparticles using an atomic force microscope.
6. Testing solid substrates using dyes. Checking the operability of the sensor element during Raman spectroscopy.

Project relevance:

Sensitive materials created using films of silver nanoparticles placed on a solid substrate are highly effective and relatively inexpensive to produce. The synthesis of nanoparticles is simple and allows for a large surface area to be obtained. The consumption of nanoparticles required to produce sensors is low. Silver nanoparticles also have high reactivity. Films made of silver nanoparticles have signal uniformity across the entire surface of the sensor element.

The sensor materials described above can be used to create sensors that can amplify the intensity of the Raman scattering signal and are used in such a modern method of substance analysis as Raman spectroscopy. SERS (surface enhanced Raman scattering) is a method



of combinational scattering in which both quantitative and qualitative analysis of a substance is performed simultaneously. It is an effective method for chemical analysis and studying the composition and structure of substances. During Raman spectroscopy, the sample under investigation is illuminated by a laser beam with a specific wavelength that is not absorbed by the sample.

Raman spectroscopy has many advantages. This method allows for non-destructive and non-contact analysis of substances. For example, it allows you to identify a substance in a transparent container without opening the packaging. As a rule, the laser used in Raman spectroscopy is harmless to the sample. Raman spectroscopy can be used to analyze liquids, powders and solid samples without the need for complex sample preparation. These qualities of the method allow it to be widely used in medicine. For example, in the chemical analysis of drugs, in the diagnosis of malignant and benign tumors, in the monitoring of cancer using readily available biological fluids, and for non-invasive examination of biological tissues.

Similar spectrometers are also used in other areas where remote analysis of substances is required (e.g., in the chemical industry, for detecting explosives from a safe distance using laser beams), as well as for studying works of art and analyzing corrosion products on the surface of artefacts. For example, when establishing the authenticity of paintings using this method, individual pigments can be identified. It is also used in the study of statues, ceramics, precious stones, for studying the chemical composition of historical documents, and in forensics for analyzing evidence.

Thus, work on the creation, study, and improvement of effective and affordable sensor materials for Raman spectroscopy, such as silver nanoparticle films, is extremely necessary and relevant. Raman spectroscopy requires many sensor elements capable of amplifying the intensity of the Raman scattering signal. In addition to Raman spectroscopy, these sensor elements can be used in electrochemistry and spectrofluorimetry.

Project interdisciplinarity:

The project involved not only chemistry but also physics and mathematics (calculating the diameter and concentration of silver nanoparticles based on absorption spectra, finding the resonance frequency for an atomic force microscope probe). Programming and electronic equipment skills were also required (working with an atomic force microscope in “Nova SPM” computer program, processing ultraviolet-visible (UV–Vis) spectroscopy readings).

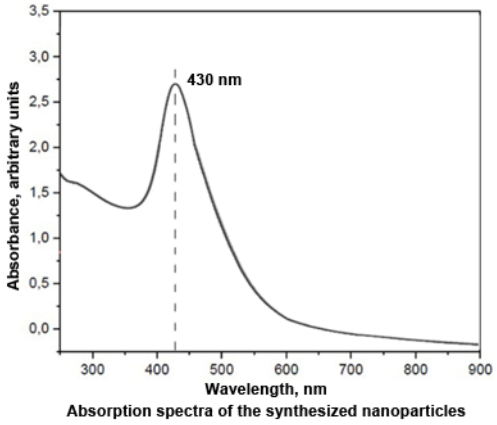
Workflow

Synthesis of AgNPs via the Leopold–Lendl Method:

The Leopold-Lendl method was used to synthesize SERS-active silver nanoparticles (AgNPs) colloids. The following reagents were used: $AgNO_3$ (silver nitrate), $NH_2OH * HCl$ (hydroxylamine hydrochloride solution) and $NaOH$ (sodium hydroxide). Deionised water was used to prepare all aqueous solutions. The corresponding solutions were added under continuous stirring to a heat-resistant flask.

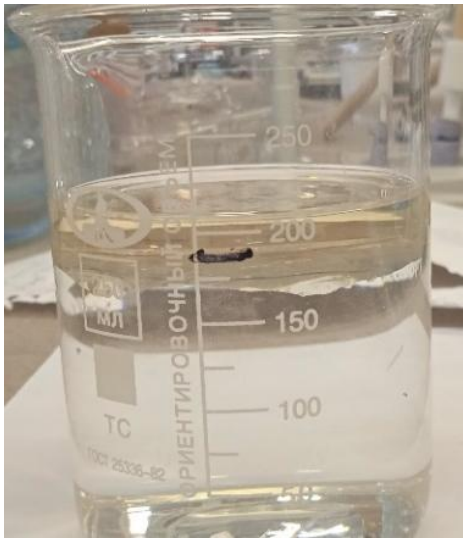
As a result, the final acidity is neutral (pH = 7). The reduction reaction proceeded instantly, within a few seconds. Silver colloids exhibited SERS activity immediately after their synthesis.

UV–Vis Spectroscopy and Calculations:



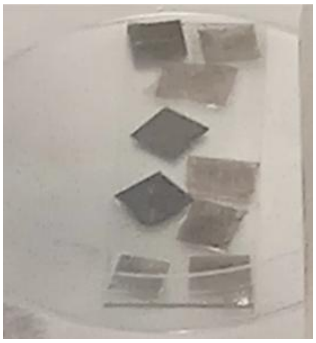
UV–Vis spectroscopy was performed on the synthesized nanoparticles, and data was obtained for calculating the reagents for the self-assembly of silver nanoparticles when combined with TTF (tetrathiafulvalene). To obtain a layer of silver nanoparticles, a solution of AgNPs with TTF was applied with a pipette to the interface between the media (water-hexane).

Self-Assembly of AgNPs:



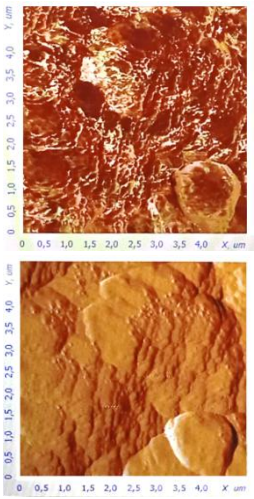
The calculated amount of AgNPs was added to 1 ml of 1 mM TTF solution, shaken until a single drop formed and the solution discolored – AgNPs self-assembled. A monolayer formed only when the volume of AgNPs was more than 2223 µl. Hexane was added to a silanised beaker with deionised water, forming an interface. The AgNPs solution with TTF was dripped onto the interface, producing a layer of silver nanoparticles.

Transfer of AgNPs Films onto Substrates:



After obtaining a layer of silver nanoparticles at the interface between water and hexane, it was necessary to transfer the resulting film onto substrates. The "aqua print" method was used: the substrates were picked up with tweezers and dipped into the phase interface where the AgNPs film had formed. After that, the substrates covered with a layer of AgNPs were placed in a Petri dish.

AFM Imaging of AgNPs Films:



The Nova SPM software was used to operate the atomic force microscope. The device was configured with the following parameters: $\mathrm{DFL} = 0.1$, $\mathrm{LF} = 0.1$, and $\mathrm{Laser} \in [26; 32]$. A resonance frequency of 319 kHz was set for the probe. In semi-contact mode, images of the film surface were obtained in 1×1 μm area. By changing the scanning speed and quality, different images were obtained; the defects detected did not exceed $200 - 300$ nm.

Conclusion

Results:

During the project, the following tasks were completed:

1. Scientific research and literature on the project topic were studied.
2. The synthesis of silver nanoparticles was successfully carried out. The average diameters of AgNPs and their concentration were determined using UV–Vis spectroscopy. The average particle size was $d = 79$ nm. Based on the compiled data, calculations were performed to determine the amount of AgNPs required to fill a specific surface area.
3. Self-assembly of AgNPs was performed and films were obtained at the interface between the media.

Summary:

Obtaining thin films from silver nanoparticles using self-assembly of particles at the interface between two media is indeed an effective and affordable method that does not require complex laboratory conditions. Thin films of silver nanoparticles placed on a solid substrate can potentially be successfully used as sensors in Raman spectroscopy, since silver nanoparticles have high reactivity and effectively amplify the Raman scattering signal.

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