High Stable Silver Nanoparticles for Sensing Applications Synthesized by Magnetron Deposition and Ion Irradiation

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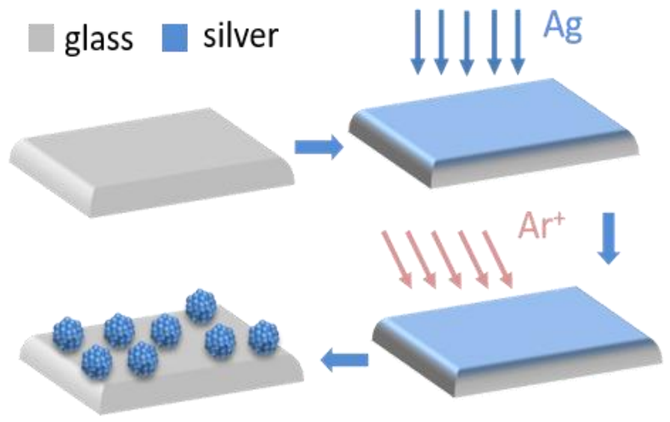
Ensembles of silver nanoparticles (NPs) with size ~20 nm deposited on glass and silica substrates using magnetron deposition and subsequent ion irradiation are studied. Optical spectroscopy demonstrated that the fabricated ensembles of silver NPs keep stable their plasmonic properties in an ambient atmosphere at least 39 days due to their monocrystalline nature. Surface-enhanced Raman scattering (SERS) from Crystal Violet homogeneously adsorbed on these ensembles is characterized using Raman microscopy. It was found that the manufactured ensembles have a strong amplification factor, and this factor is preserved for these ensembles even after more than one month of storage in the surrounding atmosphere. Hereby, by using magnetron deposition and subsequent ion irradiation it is possible to fabricate the silver NPs with stable plasmonic properties and form nanostructured surfaces to be applied in sensor technologies and SERS.

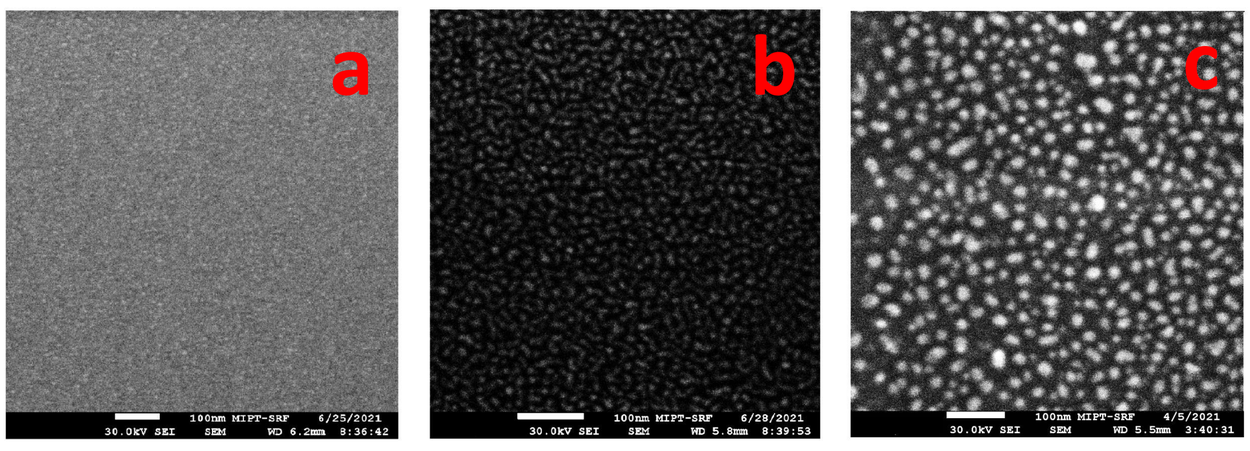
Ag NPs fabrication

The coating process is carried out in a high-vacuum chamber with preliminary pumping up to 10^{-5} Torr, followed by the synthesis in an argon atmosphere at a residual pressure of about 10^{-4} Torr. The cover glass or silica is used as a substrate. A thin coating is deposited by radio-frequency magnetron with a silver target with a purity of 99.999% are used. The discharge power is approximately 30 W. The obtained coating consists of the film with a thickness of ~20 nm. The quoted "thickness" of the silver films is the average nominal coverage values measure by the quartz oscillator. After the deposition, the argon-ion irradiation of 150 eV energy and 20 mA output current is applied to the deposited films for 120-300 seconds. The ion beam is produced by Hall-effect ion source with cold hollow cathode Klan 53-M (Platar Corp.). The introduction of ion irradiation leads to the formation of nanoparticles with an average size ranged from 10 to 20 nm depending on irradiation period.

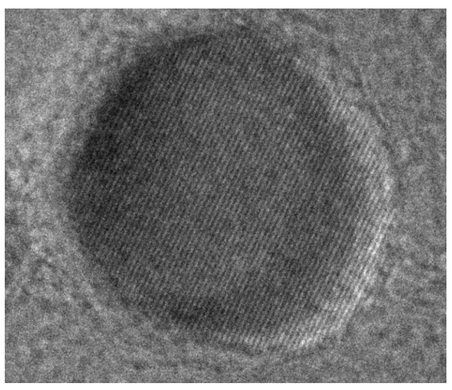


Schematic process of the fabrication of the samples

Scanning and transmission electron microscopy (SEM, TEM)



SEM images of the samples obtained at various ion irradiation periods (a – 0 sec., b – 120 sec., c – 300 sec.) are shown in the figure above. In figure (a) one can observe untreated surface of the deposited silver coating possessing ~10 nm typical roughness. Ion irradiation of the film leads to the start of the developed surface followed by the formation of separate islands and ~15 nm-sized particles (see figure (b)). Subsequent increase of the irradiation period leads to the formation of free-standing nanoparticles with ~20 nm size (see figure (c)).



TEM studies of the nanoparticles revealed high degree of their monocrystallinity. However, no preferred NPs orientation is observed: various nanoparticles situated on the substrate surface have different orientation.

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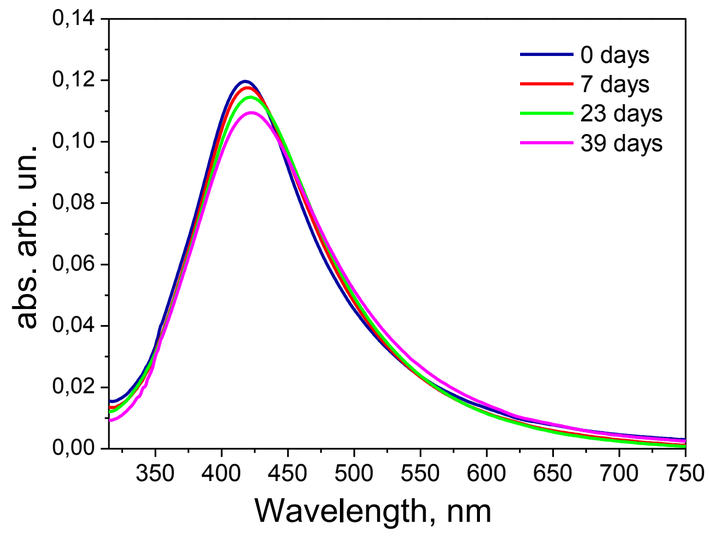
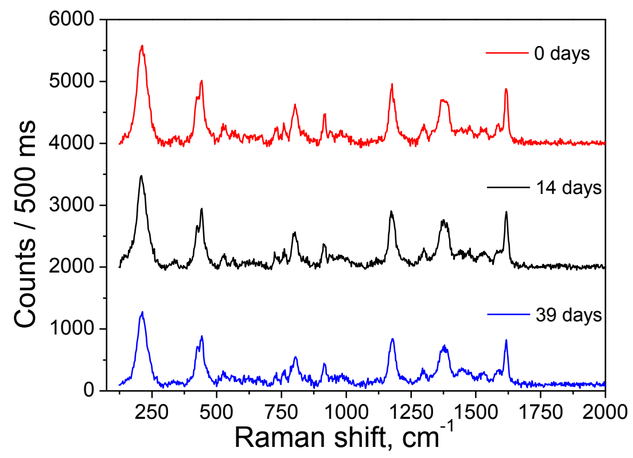
UV-Vis-NIR spectroscopy



The samples are characterized by UV-Vis-NIR spectrophotometer Agilent Technologies Cary 5000 (175-3300 nm). Optical spectra of the samples with ensembles of silver NPs presented in the figure above show the localized surface plasmon resonance (LSPR) band with a maximum at near 418 nm. The intensity and spectral position of the plasmon band is monitored for 39 days. After 7 days, the resonance band becomes slightly red-shifted and its intensity is insignificantly decreased. In the period between 7 and 23 days, the intensity starts slowly decreasing and the band continues the redshift. After 39 days, the band intensity is decreased to less than 10% from the origin intensity, thus demonstrating the good stability of the optical properties. The possible reason for the observed insignificant redshift and decrease in intensity red can be the beginning of the formation of an oxide shell due to interaction with atmospheric oxygen.

SERS



To estimate the applicability of the fabricated samples for SERS, the Raman measurements are performed. We used confocal Raman microscope Horiba LabRAM HR Evolution. The measurements are conducted with a laser wavelength 632.8 nm, integration time 0.5 sec., 100× objective (N.A.=0.90) and with the incident power ~0.3 mW. The measurements are carried out on the sample kept in an ambient atmosphere for 0, 14 and 39 days after the fabrication. Samples are covered by 10^{-6} M solution of Crystal Violet (CV) in water solution and dried under ambient conditions. The typical SERS image and spectra obtained from the sample with ensembles of Ag NPs are shown in the figure. Spectra demonstrate relatively similar intensities for the samples which were kept in an ambient atmosphere for 0 and 14 days. The SERS intensity of sample after 39 in the ambient atmosphere is a little bit (~15-20%) less. **In summary, high stability of monocrystalline Ag NPs treated by low-energy ion irradiation leads to the preservation of their plasmonic properties even after prolonged exposure to the laboratory environment.**