# Plasmonic nanocavity metasurfaces based on femtosecond laser-nanostructured patterns perspective for the enhanced optical response of organic and biological molecules


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**We study an efficiency of the application of laser-induced periodic surface structures (LIPSSs) either directly fabricated on metallic surfaces or obtained on semiconductor substrates subsequently coated with metallic gold film for highly sensitive fluorescent label-free detection and imaging of biomolecules (nucleotides) or dyes (Rhodamine 6G) at room temperature. LIPSSs at different materials were formed with irradiation from a Ti:sapphire femtosecond (fs) laser with a wavelength of 800 nm, the pulse duration ~ 150 fs at a repetition rate of 1 kHz with a mean power about 1.4 W.**


- ✓ Initially we studied gain effects at fs-laser-induced metallic structures, in particular Ag metal. The excitation of surface plasmons in the fs-laser structured metallic surfaces stimulates the enhancement of Raman signals. We achieved SERS enhancement from Rhodamine 6G (Rh6G) ($C_{28}H_{31}N_2O_3Cl$) dye adsorbed on Ag LIPSSs in comparison with an untreated surface (Fig. 1). Maximal enhancement factor up to 20 for some vibrations of Rh6G has been obtained for depicted Ag LIPSSs.
- ✓ At the next stage we designed the plasmonic cavity metasurfaces based on Ag LIPSSs and Ag triangular nanoprisms (O.A. Yeshchenko, et al. Plasmonic Nanocavity Metasurface Based on Laser-Structured Silver Surface and Silver Nanoprisms for the Enhancement of Adenosine Nucleotide Photoluminescence // ACS Appl. Nano Mater. – 2019. – **2**. – 7152-7161) that demonstrated for 5′-deoxyadenosine monophosphate (dAMP) the PL enhancement factor of 1120 at 300K. Further formed plasmonic nanocavity metasurfaces based on Ag LIPSSs combined with Au nanorods (NRs) or nanospheres (NPs) revealed 1220 times PL enhancement for dAMP on Ag-LIPSS/Au NRs metasurface. The nature of this enhancement - combined effect of the hot spots generation near the sharp edges of LIPSS and Au NRs tips and the excitation of collective gap mode of the cavity (Yeshchenko O.A., et al. Laser-Induced Periodic Ag Surface Structure with Au Nanorods Plasmonic Nanocavity Metasurface for Strong Enhancement of Adenosine Nucleotide Label-Free Photoluminescence Imaging // ACS Omega.-2020 -**5**.-P. 14030-14039).
- ✓ The next stage includes the study of an efficiency of metal-semiconductor metasurfaces based of Si/Au LIPSSs. PL spectra of Si/Au LIPSS metasurfaces demonstrate essential enhancement of PL signal in comparison with PL spectra of untreated Au film or Si surface due to the formation of spatial areas with highly intense EM field that makes designed metasurface perspective for fluorescent label-free detection of biomolecules or dyes at room temperature.

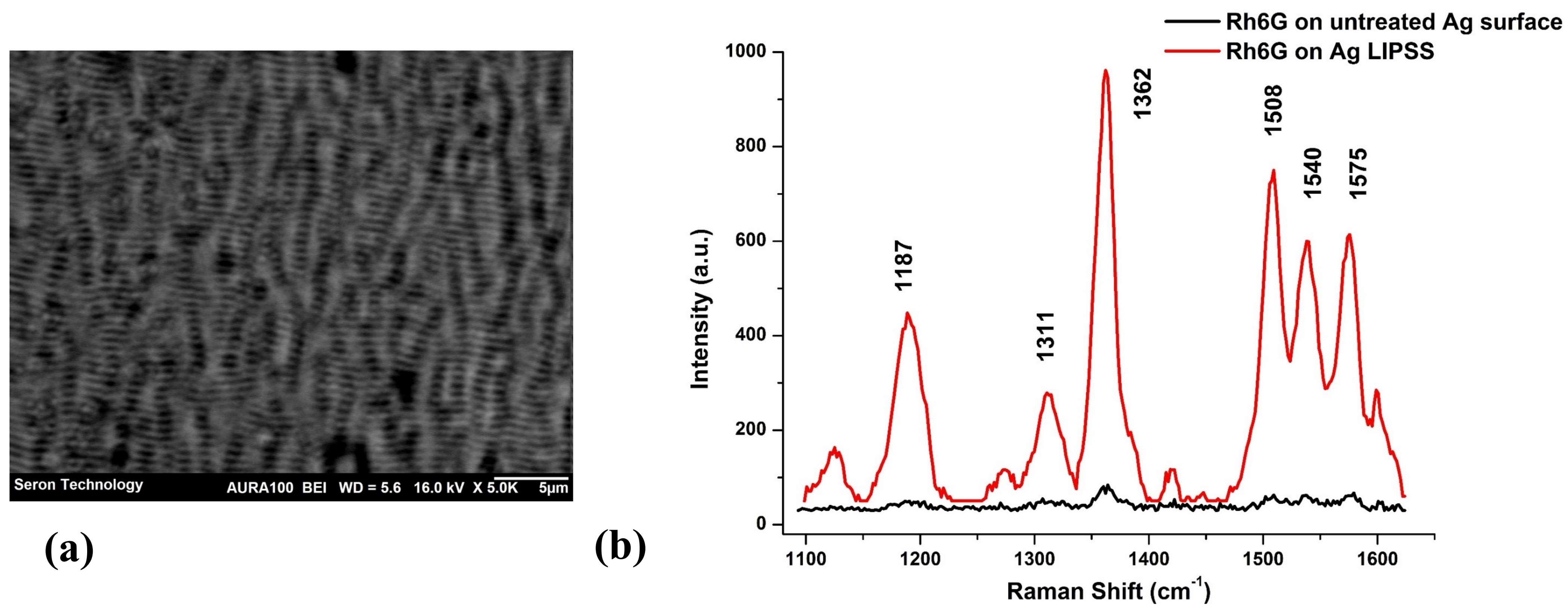
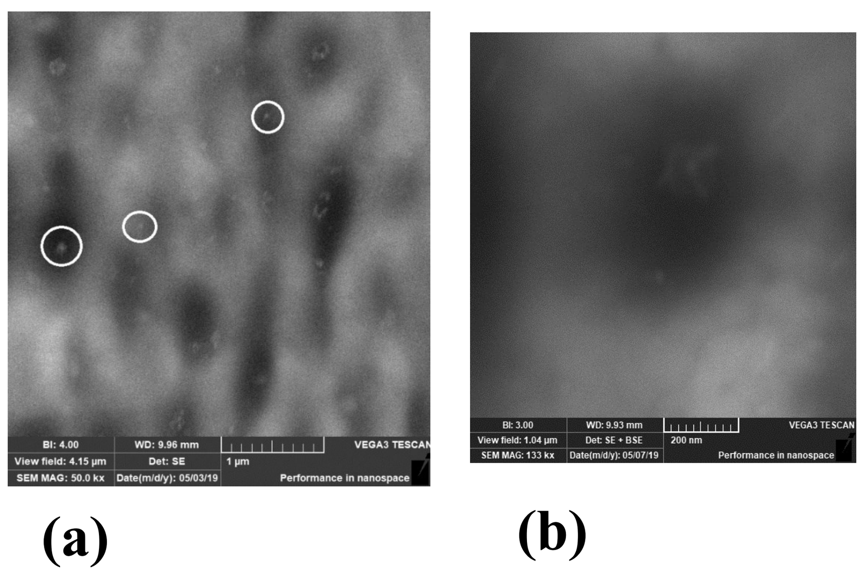



*Fig. 1: (a) SEM image of Ag LIPSSs, (b) Raman spectra of Rh6G dye (concentration $2*10^{-6}$ M) adsorbed on Ag surfaces: untreated and fs-laser-treated at the pulse irradiation energy density of 0.53 J/cm$^2$, the efficient number of laser pulses of 135; $\lambda_{exc.}$ =488.0 nm, T=300 K*



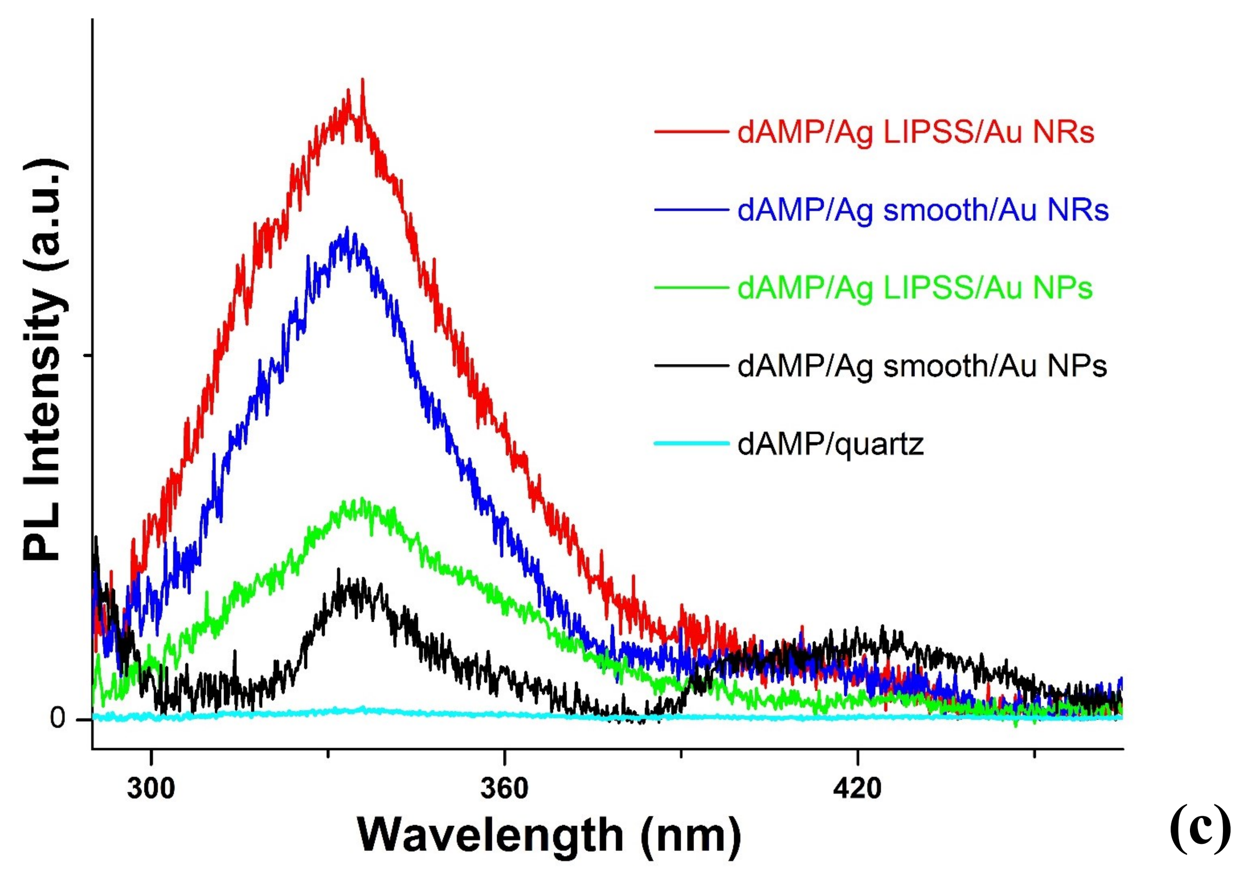
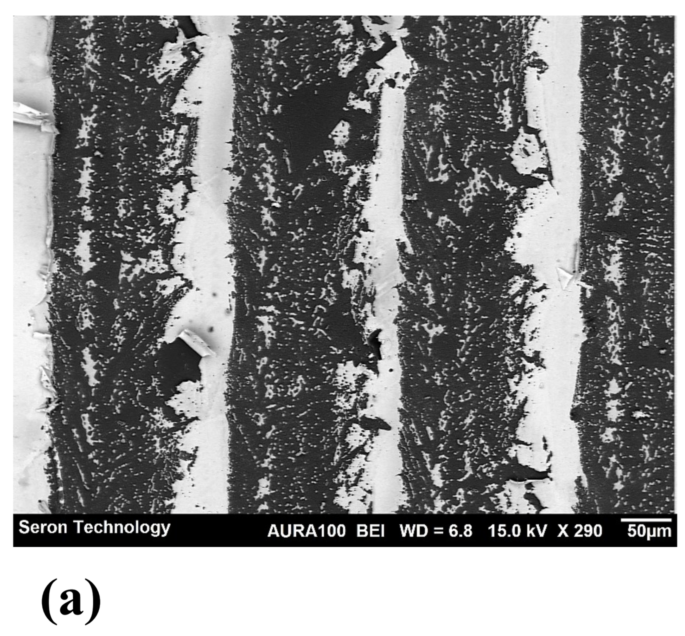




*Fig. 2: (a, b) SEM images of Ag LIPSSs with Ag triangular nanoprisms in cavities and ribs (c) PL spectra of dAMP molecules deposited on different substrates with Au nanorods or nanospheres; $\lambda_{exc.}$ = 260 nm, T=300 K*



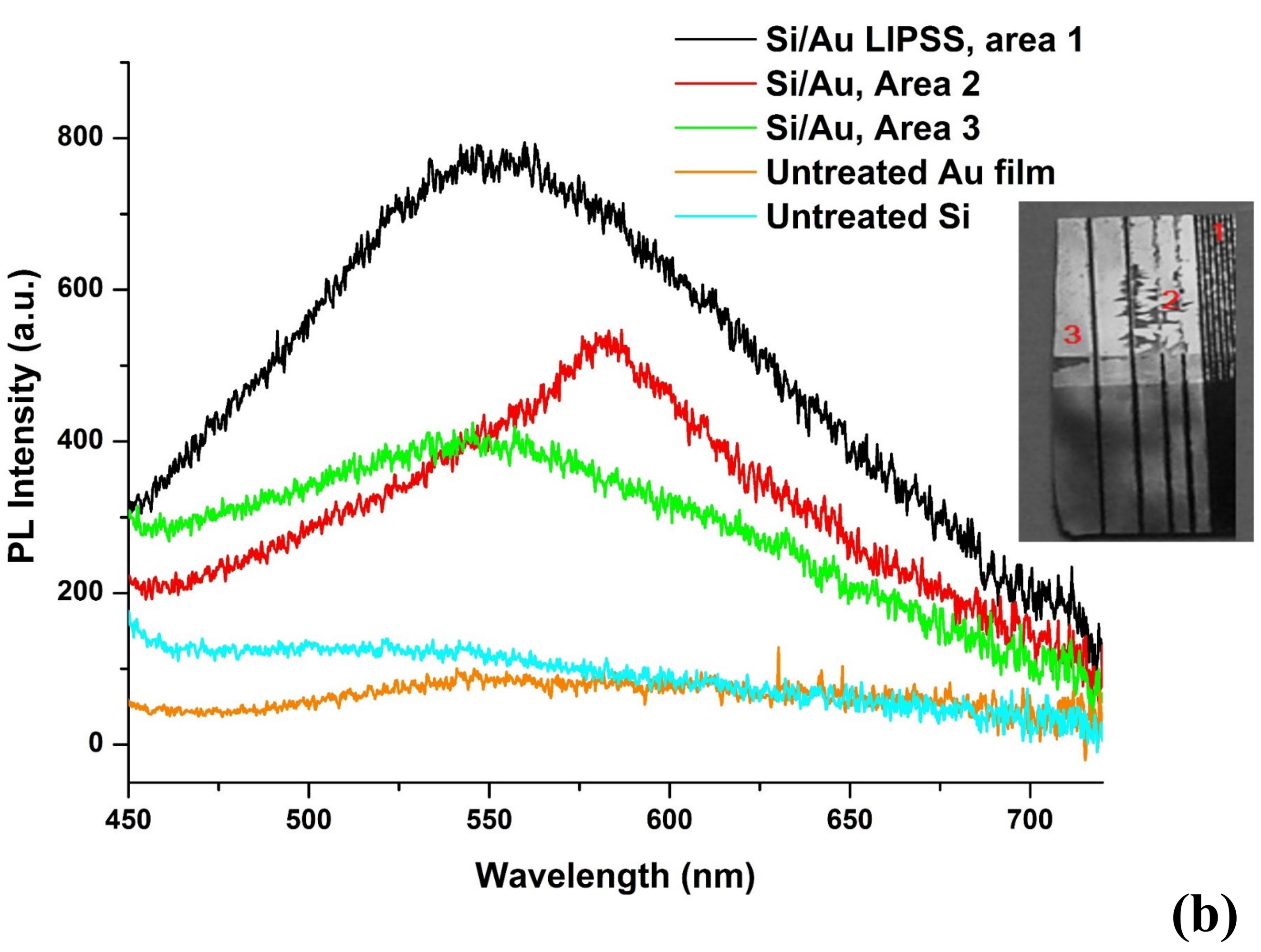




*Fig. 3: (a) SEM image of Si/Au LIPSS metasurface (area 1) formed at the pulse irradiation energy density of 0.13 J/cm$^2$, the efficient number of laser pulses of 83, (b) PL spectra of different parts of Si/Au LIPSS metasurfaces and untreated Au film or Si surface; $\lambda_{exc.}$= 405 nm, T=300 K*

***CONCLUSIONS:*** **It has been demonstrated the prospects of plasmonic nanocavity metasurfaces based on LIPSSs with noble metal NPs for an increase of the spectroscopic signals by up to several orders of magnitude in SERS or surface-enhanced fluorescence due to the crucial role of the effective excitation of plasmon gap mode and respective EM field enhancement at these matasurfaces.**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