HYBRID Ag-DYE-POLYMER NANOSTRUCTURES: FABRICATION WITH DIRECT LASER WRITING TWO-PHOTON LITHOGRAPHY AND LUMINESCENCE LIFETIME ANALYSIS

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Fabrication is a critical step for developing materials with tunable plasmonic properties. When designing nanostructures, the available fabrication techniques to produce and modulate the desired geometry and optical properties must be considered. In this study hybrid metallic-polymer nanostructured systems were fabricated with Direct Laser Writing (DLW) lithography at two photon absorption (TPA). 3D nano-arrays to exhibit additional plasmon resonance modes that are result of both horizontal and vertical coupling. 3D nanostructure coupling not only exhibits new plasmon modes, but also interesting optical phenomenon.Fabrication of hybrid nanostructures of predefined topology containing plasmonic metals is of interest in electronics and nanophotonics, for sensors designing bio-medicine, forensic, food industry, etc.

The composition of pentaerythritol tetraacrylate (PETTA) as monomer, 7-diethylamino-3-thenoyl-coumarin (DETC) as photoinitiator and a silver trifluoroacetate ($AgCF_3COO$) for photoreduction of plasmonic metal nanoparticles was used. The printing of the elements of pre-established configuration was performed using tunable Ti:Saphire femtosecond (fs) laser at 800 nm and excitation beam focusing with high aperture objective at scanning of a sample around focused laser beam with piezo stage and stepper motor stage.

Dependence of the nanoAg presence on the varied DLW parameters (laser power, scan speed) was investigated by luminescence lifetime analysis and fluorescence lifetime imaging (FLIM). The TPA luminescence was excited with fs Ti-sapphire laser at 820 nm. Luminescence lifetime data were obtained and analyzed. Lifetime of the PETTA-DETC matrix excited close to maximum TPA of DETC dye was estimated as 2.86 ns. Lifetime of reduced Ag was very short, close to IRF, and only could be estimated lower than 0.01 ns. Ag particles or clusters are visualized in FLIM via strong intensity of luminescence and short luminescence lifetime.

The results show that recovered Ag content and form can be controlled by the DLW parameters. An incorporation of Ag nanoparticles and nanoclusters in the polymer-dye matrix allows designing nanostructured systems for practical applications, and for study of nanoAg luminescence at interaction with the closest environment, particularly involving the plasmon effects, and energy transfer. Additionally, applied photosensitive composition (photoresin) is compatible for stimulated emission depletion (STED) nanolithography, a technique overcoming diffraction limit and providing the resolution in nano-range with implementation of visible laser light, utilizing fs laser at 800 nm and depletion with cw 532 nm laser [1] for 2D and 3D systems printing.

Plasmonic nano-arrays sometimes are randomly assembled into devices, in which the plasmonic effect has not been utilized effectively. To solve this problem, plasmonic applications should be implemented in a manner of "device-by-design" and in this case DLW-STED can play a significant role.

[1] A. Vitukhnovsky; D. Chubich; S. Eliseev et al "Advantages of STED-inspired 3D direct laser writing for fabrication of hybrid nanostructures," *J Rus Laser Research* **38**, 375-382 (2017).