Preparation and characterization of systems with plasmonic metal nanoparticles for fluorescence-lifetime imaging microscopy

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Luminescence of luminophores localized in a close proximity of plasmonic nanoparticles (NPs) such as Au or Ag are known to be completely or at least partially quenched [1]. However, in the case of larger distances from the metal surface a luminescence enhancement may be observed [2]. In order to investigate nanoparticle-luminophore distance effects, we focused our attention on reproducible preparation of homogeneous and well-defined model samples.

We studied systems with gold as well as silver NPs prepared by different techniques. The first set of samples were [substrate–AuNPs–spacer–luminophore] systems differing by AuNPs morphology. The substrates were microscopic cover glasses with constant thickness (specimens for fluorescence lifetime imaging microscopy, FLIM) and carbon-coated copper grids (specimens for TEM, controls). AuNPs were sputter-coated on the substrate; their morphology was controlled by sputtering time and subsequent thermal treatment. The spacer layer was created by thermal evaporation of carbon. The testing luminophores were widely used quantum dots and Ru(II) tris(2,2'-bipyridine); those were both sprayed and drop deposited onto the sample. The second set of samples comprised [substrate–AgNPs–luminophore] systems. In this case the AgNPs were prepared chemically by reduction of silver nitrate by hydroxylamine hydrochloride and in a form of a single aggregate deposited onto microscopic cover glass [3]. The testing luminophore /Ru(II) tris(2,2'-bipyridine) was drop deposited. The luminescent signal was measured immediately after deposition.

The size and the shape of Au and Ag nanoparticles were monitored by TEM and FEGSEM. We demonstrated that the combination of sputter coating and thermal treatment could yield NPs ranging from 5 nm up to several mm. The average size of the AgNPs was ~30 nm. The presence and homogeneity of luminophore on the surface was verified by TEM and EDX. Preliminary FLIM experiments of the systems with AuNPs showed quite inhomogeneous distribution of fluorescence lifetimes. Parallel TEM investigations suggested that the luminophores were deposited in multiple layers. Therefore, the different distances of luminophores from different layers might explain the observed distribution of FLIM signal. In the case of Ag NPs systems and drop deposition of luminophore, the surface-enhanced luminescence was observed.


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Fig. 1: TEM images of sputtered and thermally treated AuNPs (t. = sputtering time, thermal treatment: 450 °C/15 min).

Fig. 2: Fluorescence lifetime images and elastic scattered light images of AuNP/C/QD 510 system (A, B) and AgNP/Ru(bpy): system (C, D).