Optical properties of nanopatch antennas based on plasmonic nanoparticles and ruthenium complex

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Abstract. In this work, a significant reduction (up to 7 ns) of the excited states lifetime of the Ru dye (with a decay time of 850 ns) in an inhomogeneous «aluminium – silver nano-prism system (nano-patch antenna, NPA)», as well as an increase in the photoluminescence emitter to 2-3 times. The increase in the spontaneous emission rate of this substance is caused by the Purcell effect. The Purcell coefficient for the emitter in the cavity with hexagonal silver particles was 120. This decrease in the spontaneous emission decay time in the nano-patch antenna configuration is associated with an increase in the local density of photon states in the plasmon resonator, which increases the probability of a spontaneous transition from the excited state of the emitter. The results obtained by shortening the spontaneous emission time and increasing the intensity of the emitter radiation in a nano-patch antenna show possible prospects for using quantum dots and individual molecules with shorter luminescence times in nano-patch antennas. Such nano-patch antennas can form the basis for creating compact high-speed optical devices. Modeling in the mathematical package Comsol Multiphysics showed that the maximum values of the Purcell factors can exceed 10⁷ in the NPA.

1. Introduction

Optical nanoantennas convert far-field radiation into localized energy and vice versa. They provide the ability to control and process optical fields at a nanometer scale, and seem promising for improving the performance and efficiency of photodetection, light emission and sensing [1-4]. Although many properties and parameters of optical antennas are similar to their radiowave and microwave analogs, they have important differences due to their small size and resonant properties of nanostructures. Due to the importance of the optical frequency range, various structures and mechanisms of nanoscale antennas operation have become relevant for discussion in the last 15-20 years. This is due to the fact that the characteristic dimensions of the antennas of the optical range is determined by the effective radiation wavelength, on the order of hundreds of nanometers, which causes the technological problems of creating such small devices [5-11].

In recent years, a significant interest of the scientists was drawn to plasmonic nanopatch antennas (NPAs) [12, 13]. NPAs consist of plasmonic nanoparticles and metal films separated by dielectric layers [14-17]. In contrast to the bow-tie antennas [6], NPAs are created using rather simple film-processing technologies and the thicknesses of their layers can be controlled with a nanometer precision.
In this paper, we demonstrate results of fabrication and investigation of the NPA with hexagonal and pentagonal silver nanoparticles matched with the ruthenium dye (Ru dye) wavelength.

2. Results

The following samples were fabricated: glass/Ru dye, glass/aluminum/Ru dye/nanoparticle (NPA). Aluminum substrates were fabricated by thermal evaporation in vacuum. The layers of the ruthenium dye and silver particles were deposited by spin-coating. A schematic diagram of the obtained patch-nanoantenna and its parameters are shown in Figure 1(a). NPA consists of a glass substrate, an aluminum layer (100 nm) coated with an aluminum oxide film (3 nm), a ruthenium layer (30 nm) and the silver nanoparticles: hexagonal nanorism (d = 60 nm, h = 9 nm) or pentagonal nanorod (d = 100 nm, h = 40 nm).

![Figure 1.](image)

We show in Figure 1(b) the experimental transmission spectra of silver nanoparticles in water solution. It can be seen that the plasmon resonance of hexagonal nanoprisms is $\lambda_h = 540$ nm, the solution of pentagonal nanorods has two plasmon resonance maxima $\lambda_{p1} = 420$ nm, $\lambda_{p2} = 650$ nm. These wavelengths are determined by the geometry and material of the nanoparticles.

We performed numerical simulations using finite-element method (FEM). The commercially available software package (Comsol Multiphysics) is used. In modeling we used following parameters: for each NPA, a dielectric spacer with a refractive index $n = 1.7$ is sandwiched between the Ag nanoparticle and the Al/Al$_2$O$_3$ thin film; the NPA is supported by a glass substrate ($n = 1.47$). The optical constant of Ag is obtained from the literature [18]. The thickness of spacers was 30 nm and Al films were set as 100 nm. For the scattering study, a normal incident light is illuminated from the top of the NPAs and back-scattered light is collected with a two-dimensional (2D) frequency domain power detector at the top. For investigating of the radiation properties of the NPA, an electric dipole emitter is placed inside the spacer. For modeling the plasmon nanoparticles edges were not rounded.

The Ru dye luminescence spectrum is in the visible red region with a maximum at a wavelength of 620 nm and a peak width of about 50 nm (inset of Figure 2(a)). The geometry and size of the particles mainly affect the plasmon resonance of the nanoparticles. The obtained scattering spectrum of single silver nanoparticles in NPA (Figure 2(a)) shows that the region of maximum scattering is in the red region, with the maximum scattering peak for hexagonal nanoprisms at a wavelength of 630 nm, and for pentagonal nanorods at 635 nm. The hexagonal particle has one peak, and the nanorod has two peaks associated with the short (40 nm) and long (90 - 100 nm) sides of the particle. The second resonance peak is in the UV region at a wavelength of about 450 nm, which is of no interest in our work. The calculations of EM field distribution show that the highest local field enhancement (~ 50) is observed at the corners of the hexagonal prism (Figure 2(b)) and the pentagonal nanorod (Figure 2(c)). For different
NPAs, the difference in the resonant wavelengths arises from the variation in the effective lengths corresponding to the Fabry-Perot resonances [19].

The luminescence decay times were studied on a scanning luminescent confocal microscope for the following cases: Ru-complex on glass and in NPA (Figure 1(a)). The luminescence decay curves are shown in Figure 3. From the behavior of the luminescence decay curve in NPA with plasmonic nanoparticles can be seen the effect of shortening the decay time of the ruthenium spontaneous emission and an increase the integrated luminescence intensity in comparison with similar parameters for the ruthenium region on glass is observed. We show a significant (up to 7 ns) decreasing the lifetime of the excited states of the Ru dye (with a decay time of ~ 850 ns) placed in NPA. This effect of increasing the speed of spontaneous emission of a substance is explained by the Purcell effect. The life-time decreasing is characterized by the Purcell factor [5]:

$$F_p = \frac{\gamma_{sp}}{\gamma_{0}}$$

where \(\gamma_{sp}\) – speed of spontaneous emission of the emitter in the resonator and \(\gamma_{0}\) – speed of spontaneous emission of the emitter in free space. The Purcell factor for Ry dye in the NPA with pentagonal nanorods and with hexagonal silver nanoprisms was 100 and 120, respectively (Figure 3). The speed of the spontaneous emission of an emitter depends both on the speed of non-radiation, which are caused by metal quenching of the radiation, and radiation processes.

We calculated the distributions of the Purcell factors with respect to the distance to a aluminium surface of the vertically oriented electric dipole in the NPA gap (Figure 4 (a)). For the NPAs with the hexagonal nanoprisms and the pentagonal nanorods, the maximum Purcell factor near the surface of nanoparticles was up to 10^4. We also calculated the radiation efficiency for the considered NPAs. It was found that averaged radiation efficiency for the NPA with hexagonal nanoprisms was 0.3 and for the NPA with hexagonal nanorod was about 0.5 (Figure 4 (b)).

![Figure 2](image-url)

**Figure 2.** (a) – Calculated scattering and absorption spectra of plasmonic nanoparticles: hexagonal nanoprisms, and pentagonal nanorod; inset shows excitation and luminescence spectra of Ru dye. In-plane distributions of EM fields in NPA at resonant wavelength of incident light \(E_0\) for (b) - hexagonal nanoprisms and (c) - pentagonal nanorod. Polarization of incident light is shown by arrows.
Figure 3. Time decay curves of the Ru dye luminescence in different cases: on a glass substrate, in the NPA with a pentagonal nanorod, in the NPA with a hexagonal nanoprism.

Figure 4. Distribution of the Purcell factor (a) and radiation efficiency (b) from the dipole distance to a metal surface in the gap of the NPA: for hexagonal nanoprism and for pentagonal nanorod. The arrows indicate the location of the dipole in the NPA gap.

3. Conclusions
The growth of the radiative power of an organometallic system was demonstrated experimentally. The averaged Purcell factors were 120 for the NPA with hexagonal nanoprism and Ru dye film. We shown that the maximum Purcell factor were obtained for the emitter placed at distance less than 10 nanometers from the surface of nanoparticle. For the dipole is located near the metal surface, the radiation efficiency drops to 0, which is caused by metal quenching. It’s the important problem of plasmonic nanoantenna.

NPA can be used for creating small (about 10 nm) and high-speed (1 THz) optical devices. NPA with a ruthenium complex is of interest for photovoltaic applications [20].

Acknowledgments
The authors are grateful to Dr I.V. Taydakov (P.N. Lebedev Physical Institute, RAS) for synthesizing tris(2,2'-bipyridine) ruthenium(II) hexafluorophosphate and to V.V. Sychev (P.N. Lebedev Physical Institute, RAS) for useful discussions. The technological part of this work was supported by the Russian Science Foundation (project No. 15-19-00205), and the experimental part was supported by the Russian Foundation for Basic Research (under projects Nos. 18-02-00811, 17-02-01408, and 16-29-11805).

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