Nonlinear optical properties of Sponge Si/Au nanoparticle

Artem Larin, Eduard Ageev, Anna Shiker, Alexandre Nomine, Sergey Makarov, Dmitry Zuev
Faculty of Physics and Engineering, ITMO University, 49, Kronverksky pr., 197101, Saint-Petersburg, Russia
E-mail: artem.larin@metalab.ifmo.ru

Abstract. Plasmon sponge nanostructures have occupied a special role in the field of plasmonics and nanophotonics: sensors and advanced source of white emission. If the pores of a golden spongy nanostructure are filled with silicon, the result will be a promising source of broadband radiation with high efficiency due to the localization of the field by a structure with a high surface-to-volume ratio. This paper presents the results of photoluminescence generation with multiphoton absorption and second-harmonic generation obtained from hybrid sponge Si/Au nanoparticles. The particles have been fabricated by femtosecond laser ablation at room temperature in the air. Experiments have shown the ability to generate broadband photoluminescence in the range of 500 – 800 nm (0.93 eV). The obtained results can be applied for creation of white light luminescent metasurfaces and advanced nanophotonic spectroscopy devices.

1. Introduction
Plasmon sponge nanostructures occupied a special role in the field of plasmonics and nanophotonics. All plasmon structures exhibit a high localization of the field. However, the difference between sponge and solid plasmon nanoparticles lies in the large value of the ratio of the surface area to the particle volume. Therefore the sponge nanostructures can be used for a more efficient radiation enhancement for a larger volume [1]. A good example is a combination of silicon with sponge nanostructures for the amplification process, which has promising nonlinear optical properties [2]. In spite of this fact, there are plenty of open questions related with fabrication process as well as optical properties of this type of structure.

This paper presents the opportunity of obtaining gold sponge nanoparticles (NPs) with silicon inclusions using the femtosecond laser. The results of an experimental study of nonlinear optical properties of sponge particles are demonstrated.

2. Results and discussion
2.1. Fabrication process
The synthesis process was carried out using the femtosecond laser ablation method [3] of a two-layered Si/Au film with thicknesses of 90 nm and 15 nm, respectively. Synthesis was performed at room temperature (294 K) in air on the silica glass substrate. In this case, particles with a diameter of tens to several hundred nanometers are obtained.
Figure 1. (a) NP image in scattered, naturally polarized light; a line of dense particles corresponds to the ablation path. (b) Scattering spectrum of a sponge NP.

2.2. Experimental setup
A confocal microscope system with two coaxial optical channels is used to collect the radiation (M = ×10, NA = 0.26) and a signal from the sample (M = ×50, NA = 0.42) and to pump photoluminescence (PL) and second harmonic generation (SHG) (performed at room temperature). The nanoparticles were pumped using a source of femtosecond pulses TeMa 150 (Avesta Project) with an emission wavelength of 1047 nm (FWHM = 6 nm), a pulse duration of 160 fs and a repetition frequency of 80 MHz. The average output power was adjusted with an attenuator in the range of 40 - 160 mW. The received signal, passing through the system of cut-off filters, was decomposed into a spectrum by a LabRam (Horiba) monochromator and detected by a CCD camera. A set of filters 14DM–1HR–15–0–1 (Standa) and NF03–532/1064E–25 (Semrock) was used to measure the PL spectra in a wide range, the second set of filters 14DM–1HR–15–0–1 (Standa) and Green–Blue–Glass–25 (GOST 9411–91, Colored Optical Glass) was used for a narrow spectral range. The spectral range of 519 - 549 nm was omitted in Fig. 2(a), because the filter NF03–532/1064E–25 cuts out this area. The side channel (M = ×10, NA = 0.28) was used to obtain the scattering spectra by the dark field (DF) method, the optical axis of which is directed at an angle of 68 degrees relative to the signal detection channel. A halogen lamp with naturally polarized radiation was used to measure the scattering spectra.

2.3. Optical measurements
Nanoparticles have been obtained on a silica glass substrate by laser ablation in the forward transfer scheme. During ablation, a pattern has been obtained on the substrate from a bunch of ablated particles, in accordance to laser beam movements along the surface of a two-layered Si/Au film. Exposure of the film under the action of laser radiation results in local melting of both films. Next, the products of melting was transfered onto the surface of a silicon glass substrate, precipitating in the form of spherical-like particles [3]. Therefore, a little apart from the ablation path, one can observe single particles (Fig. 1(a)) that can be measured in a confocal microscope system. Thus, hybrid nanoparticles with a sponge-like gold structure have been obtained, the pores of which are filled with polycrystalline silicon. Although the external shape
of the nanoparticle is close to the geometry of the sphere and their radii can roughly coincide, each spongy structure is unique, which means that the scattering spectra for each particle can be radically different. Within the framework of this work, the results have been presented for only one particle, the scattering spectrum of which are presented in Fig. 1(b).

When the system was excited by femtosecond radiation, broadband radiation (line width at half maximum was about 300 nm or 0.93 eV) with a narrow band at a wavelength of 523.5 nm has been detected at the output (Fig. 2(a)).

In the case of broadband radiation, the non-linear optical effect of the third-order susceptibility plays a key role. This is demonstrated in the form of three-photon absorption at a length of 1047 nm by the structure [4], which in turn excites electron–hole pairs in silicon. During the experiment it was also revealed that the maintained dependence of the PL spectra at different values of the laser power remains up to ≈180 mW (Fig. 2(b)). After exposure to a given power, the spectrum losses stability and begins to change with time. When returning to low powers, the coincidence of the spectra is no longer observed. This process can be attributed to the heating of NPs, which probably leads to a restructuring and partial recrystallization of silicon, as well as to a change in the optical properties of NPs.

The case of a narrow band at a wavelength of 523.7 nm is attributed to SHG in silicon (Fig. 3(a)). Assuming that the processes of PL and SHG proceed independently of each other, the experimental spectrum can be considered as the sum of two radiating processes. This allows us to observe the dependence of SHG on the average power of the exciting radiation (Fig. 3(b)). The dependence of the maximum SHG intensity on the power in the log-log scale is approximated by a straight line, the slope is 1.59. In the considered range points overlap quite well with the straight line and a slight divergence of points can be attributed to the mechanical shifts of the optical elements over the time. As in the case of PL, the SHG intensity began to deviate from the initial approximating straight line by a noticeable change. The reason for determining the lower power range is chosen because it is possible to distinguish the signal from noise from a value of 40 mW.

Figure 2. PL measurements for a sponge NP. (a) PL spectrum in a wide spectral range with an average pump power of 50 mW. (b) PL spectra for different average powers.
3. Conclusion
The work provides the results of using the femtosecond laser ablation method of a two-layer Si/Au film to produce hybrid sponge-like gold particles, the pores of which are filled with silicon. These particles showed the ability to generate broadband photoluminescence within the wavelength range of 500 - 800 nm (width of about 0.93 eV, counting from points on the half of the maximum intensity) and the generation of the second harmonic. At the same time, the spectra remains stable up to power values of ≈180 mW. At the power 180 mW and higher, the process of thermal modification of the structure occurs, leads to a change in the structure of the gold sponge and recrystallization of silicon. This structure can be used in the field of nanophotonics, broadband near-field microscopy and information recording elements.

4. Acknowledgments
The works on the nanostructures fabrication as well as scattering and photoluminescence studies were supported by the Grant of the President of the Russian Federation MK-3669.2019.9. Nonlinear experiments were supported by the Ministry of Education and Science of Russian Federation (Project 2.2267.2017/4.6).

5. References
[1] D. Wang and P. Schaaf. Advances in Physics X, 3(1):1456361, 2018.
[2] S. V. Makarov, I. S. Sinev, V. A. Milichko, F. E. Komissarenko, D. A. Zuev, E. V. Ushakova, I. S. Mukhin, Y. F. Yu, A. I. Kuznetsov, P. A. Belov, I. V. Iorsh, A. N. Podshubny, A. K. Sambushev, and Yu. S. Kivshar. Nano Letters, 18(1):535539, 2018.
[3] D. G. Baranov, D. A. Zuev, S. I. Lepeshov, O. V. Kotov, A. E. Krasnok, A. B. Evlyukhin, and B. N. Chichkov. Optica, 4(7):814–825, 2017.
[4] R. Mejard, A. Verdy, M. Petit, A. Bouhelier, B. Chuzel, and O. Demichel. ACS Photonics, 3:1482, 2016.