Up-conversion photoluminescence specificity of a hybrid sponge nanostructures

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Abstract.
Over the past decades, silicon is proved to be as a promising material for the development of devices in the fields of nanophotonics and optoelectronics. However, the material so popular at the current time did not find its application in nanoscale radiation sources due to the indirect bandgap of the semiconductor, which leads to low quantum efficiency. This work represents experimental results on the features of the silicon up-conversion photoluminescence enhanced by the optical resonances of the plasmonic nanosponge. The internal configuration of the nanostructure was confirmed by scanning transmission electron microscopy. The optical characterisation was provided by the dark-field spectroscopy, up-conversion photoluminescence generation and life-time measurements. The such new nanostructure type is promising for the development of nanoscale sources of broadband radiation and other applications of silicon photonics.

1. Introduction
The need for nanoscale broadband light emitters is essential for such areas as optical chip design, bioimaging, and sensing. Unfortunately, silicon has not become particularly popular in this field due to the indirect bandgap, since it gives a low quantum efficiency of radiative recombinations. In early works [1, 2, 3], which were devoted to the study of the silicon up-conversion photoluminescence (PL), the key role of resonances for a PL generation was shown. The simplest geometry for modeling properties and interpreting processes of interaction with electromagnetic radiation and for the fabrication is the nanosphere (NSph). The intrinsic resonances of the silicon NSph make it possible to enhance the field of the exciting radiation and also to increase the PL output signal. Thus, the shape of the PL spectrum curve directly depends on the shape of the enhancement factor one. Also, the intrinsic resonances of silicon are spectrally narrow, that is why silicon is not promising for the design of a nanoscale source of broadband radiation. This problem can be solved by using plasmonic nanosponges in combination with silicon. There are two key features of plasmonic nanosponges rising a special interests of special interest to such kinds of structures [4]. The first one is the high value of the surface-to-volume ratio that contributes to high electromagnetic field enhancement. The second one is the multiple localized plasmon resonance that one structure can maintain resonances at a wide spectral range. By filling plasmonic nanosponges with high refractive index semiconductor, a significant enhancement of multi-photon processes can be obtained [2, 3].
In this paper, we experimentally demonstrated the effect of the plasmonic nanosponge resonance on the output up-conversion PL of the silicon through life-time measurements. Such system representing a plasmonic nanosponge, the pores of which are filled with crystalline silicon grains, will be referred to as a hybrid sponge nanostructure (HSN).

2. Experimental setup

2.1. Fabrication
The Au-Si nanostructures were fabricated using the method of femtosecond laser ablation of a bi-layer film at the room temperature. The process of ablation was carried out with the TEMA-150 system as the source of femtosecond laser pulses with the wavelength of 1047 nm, spectral width of 7 nm, the pulse duration of 150 fs at the rate of 1 kHz and pulse energy of 50 nJ. Laser beam was focused using the Mitutoyo Plan Apo NIR Infinity Corrected Objective (10×, NA = 0.26). The Au-Si bi-layer film (15 nm and 60 nm, respectively) was used as the target (donor substrate) for laser pulses. To study the internal configuration of HSN by the scanning transmission electron microscopy (STEM) method, special metal grids were used as an acceptor substrate. Its made of copper with a thin carbon layer. Substrate of transparent silica glass was used as an acceptor substrate in the case of optical measurements.

2.2. Internal configuration characterisation
The HSN inner configuration was studied by the STEM methods: high-angle annular dark-field (STEM-HAADF) and energy-dispersive spectroscopy (STEM-EDS). A JEOL – ARM 200F Cold FEG TEM/STEM setup (200 kV operational voltage) was used with a spherical aberration probe corrector (0.078 nm resolution).

![Figure 1](image.png)

**Figure 1.** (a) Typical STEM-HAADF image of the HSN. (b) HRTEM image of the HSN from (a). (b) FFT of the considered area on the HSN (red square, see (b)) under electron beam incidence. (d-e) STEM-EDS map images, describing the spatial distribution of Si and Au atoms in the volume of the HSN. The presented nanostructure shows the following characteristics: particle diameter of ~186 nm, average pore size ~30 nm, 61at.%Si, and 39at.%Au.

2.3. Optical measurements
The PL measurement was performed at the room temperature on a confocal microscope system, consisting of two coaxial optical channels. The Mitutoyo Plan Apo Infinity Corrected Objectives were used to localize pump (NIR, M = ×50, NA = 0.42) and collect radiation from the sample (VIS, M = ×100, NA = 0.7). TEMA-150 system was used as the pump source at the repetition frequency of 200 kHz. The signal from the sample was spectrally decomposed with a LabRAM monochromator and collected with a CCD camera. To investigate the scattering spectra during
PL measurements, the dark-field microscopy was performed. Dark field optical channel was set at 68˚ relative to the pump optical axes. The Mitutoyo objectives were used for excitation (M = x10, NA = 0.28) and detection (M = x100 and NA = 0.70) of scattered signal. The sample was exposed with a halogen lamp and the scattered light was detected and spectrally decomposed by LabRAM monochromator.

Life-time measurements were carried out at the room temperature with time-correlated single photon counting (TCSPC) method using single-photon avalanche diode (50 ps timing resolution) to detect signal decay over time in the spectral range of 400 - 900 nm. The excitation was realised with a femtosecond laser with repetition frequency of 200 kHz. Picoharp 300 TSCPC module was used to detect the luminescence, and make synchronization with laser trigger.

![Figure 2. Optical properties of the HSN. (a) PL and DF spectra of the HSN. (b) Dependence of the PL intensity on the excitation intensity in the log-log scale. Numbers in the legend frame represent the order of the approximation polynomial (blue dashed line). (c) PL decay for the HSN. Inset: dependence of the fast and slow components of the PL decay of the HSN as a function of the pump intensity.](image)

3. Result and discussion

The HSN were fabricated as the result of femtosecond laser ablation (Fig. 1a). High energy laser pulse induced melting of a bi-layer Si/Au film on an acceptor substrate resulting in sphere-like nanostructures with diameters varying from tens to hundreds nm in the diameter [3]. The typical content of silicon atoms, which was determined through the EDS method (Fig. 1d-e), exceeds the concentration at the point of the eutectic (~18.6% [5]). For this reason, the formed liquid droplets of the solution of Au-Si atoms starts with the process of silicon nucleation and the growth of crystalline silicon grains. These grains are uniformly and chaotically distributed in the volume of the nanostructure. The formation of the structure is completed by the Au solidification. In this case, the final structure is a plasmonic sponge, the pores of which are formed by crystalline silicon grains. The chaotic arrangement of the last leads to the formation of an Fast Fourier Transform (FFT) of the TEM image close to the structure of a polycrystalline material (Fig. 1c).

As it was shown in early work [4] plasmonic sponges having the same characteristic parameters (such as average pore size, porosity, outer diameter) possess unique linear scattering spectra. The fact that multiple localized plasmon resonance covers a wide range of wavelengths remains unchanged. For this reason, optical measurements of HSN linear scattering and their PL spectrum are demonstrated strictly for one particle.
The HSN with nanoscale size has resonances that are located in the visible spectral range (Fig. 2a). And it is possible to obtain an up-conversion PL response from HSN when it is irradiated with femtosecond laser radiation at the wavelength of 1047 nm. Obtained PL spectrum cover entire visible range and partly near-IR. Comparison of the scattering spectrum with the PL spectrum demonstrates a correlation between the shape of the PL spectrum and intrinsic resonances of the nanostructure (the coincidence of local maxima in the scattering and PL spectra). This fact is consistent with the results from [1] where the correlation of the output PL spectrum of the silicon sphere with the structure gain spectra was shown.

The dominant contribution to broadband radiation of a HSN is a multi-photon absorption. It is lead to optically-induced electron-hole plasma caused by the plasmon-assisted transitions under high-intensity excitation [2]. The studies of the PL intensity dependence on the excitation wavelength in the log-log scale (Fig. 2b) demonstrate that the dominant processes to generate broadband PL are two- and three-photon ones. This was determined taking into account the slope of a straight line in the log-log scale (~2.37), which in turn is the degree of polynomial approximation.

The hot carriers are short-living and plasmon-assisted transitions are contributing into a sub-nanosecond ($\tau_{fast} = 0.076$ ns) exponential decay. In turn, the long-living PL ($\tau_{slow} = 0.317$ ns) we treat as the defect-supported transitions. The time scales are smaller in comparison with the work [1] ($\tau_{slow} = 1.740$ ns, $\tau_{fast} = 0.052$ ns). It can be explained by the influence of the plasmonic nanosponge, which decreases the output PL lifetime due to the Purcell effect. The considered feature is typical for the resonant plasmonic nanostructures [6]. The absence of a dependence of the PL decay on the pump intensity can be explained by relaxation through defects (see inset to Fig. 2c).

4. Conclusion
We have experimentally demonstrated the features of up-conversion PL of silicon in the HSN. It is based on two- and three-photon absorption of femtosecond laser excitation at the wavelength of 1047 nm. The geometry of the HSN was determined by STEM methods. The resonance properties of a plasmonic nano-sponge have a key influence on the PL output spectrum, which correlates with the linear scattering spectrum curve in the dark field geometry. Although, plasmonic nanosponge resonances affect the PL decay dynamics and lead to the decreasing of it in comparison with an intrinsic resonance of silicon NSph. Since the PL is based on a defect-support transitions, life-time changes are negligible and power independent. The study of HSN can open a new development designs of broadband radiation sources in nanoscale, expand the element base of structures for sensorics and catalysis.

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6. References
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