Supporting Information:

Split Hole Resonator: A nanoscale UV light source

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Importance of gold monocrystallinity for efficient THG

The single crystallinity of the nanofilm on the atomic level is of fundamental importance. First, this provides control the nanostructure geometry with a high spatial accuracy (in polycrystalline films, the nanostructure geometry accuracy is defined by the size of gold crystals and is in the range of 20 - 50 nm). Second, unlike polycrystalline films, there are no losses related to the scattering of electrons at interfaces between nanocrystals, the

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characteristic size of which is 20 - 50 nm. The latter circumstance yields large enhancement amplitudes of local fields near nanostructures.

We performed THG experiments with SHR nanostructures made in Au nanofilm of different quality: (a) polycrystalline nanofilm, (b) monocrystalline nanofilm (from PHASIS, Geneva, Switzerland). In both types of nanofilms nanostructures of identical size were created with use of the ion-beam lithography method using a tightly focused beam of Ga ions. Two types of nanostructures were made: (1) nanoslits, (2) split-hole resonators. Nanoslits were made to characterize quality of ion beam milling method. SHR nanostructures were created to discover THG process. Figure S1 present SEM image of nanoslits created in polycrystalline (a) and monocrystalline (b) gold films. As it is clearly seen from the figure, nanocrystals in the polycrystalline gold film severely limit accuracy of ion-beam lithography. While use of monocrystalline nanofilm provides control of the nanostructure geometry with a high spatial accuracy: better than 2 nm. We performed measurements of THG efficiency from identical SHR nanostructures made in both types of Au nanofilms. Two main differences were measured: (1) spectral emission, (2) damage threshold intensity.

Figure 1: SEM image of a slit-type nanostructure made in: (a) polycrystalline Au film, (b) monocrystalline Au film.

The emission spectrum of the SHR nanostructure made in polycrystalline Au consists

of narrow peaks, corresponded to the third harmonics of the excitation radiation, and a broad radiation band, which covers the spectral range from 360 nm to longer than 500 nm. Intensity dependence measurements show that this broadband radiation is a result of two-photon photoluminescence process (2PPL). On the other hand, emission spectrum of SHR nanostructures made in monocrystalline nanofilm contained only signal related to the THG process. The spectral measurements are explained by dramatic size-dependence of 2PPL efficiency.¹⁻⁵ Presence of nanocrystals in polycrystalline nanofilm makes nano-sized corrugations in SHR nanostructures. Namely these corrugations are origins for the spectrally broad 2PPL emission. Recently the same behavior was already measured in THG experiments with SHR nanostructures excited by laser radiation at 1550 nm wavelength.⁶

We have found damage threshold for SHR made in polycrystalline nanofilm as high as 1.6×10^{11} W/cm². No threshold was measured for SHR nanostructure made in monocrystalline nanofilm with use of laser light intensity up to 8.6×10^{11} W/cm². We believe that high losses in the polycrystalline film compared to monocrystalline film (the losses related to the scattering of electrons at interfaces between nanocrystals) are responsible for faster heating of the nanofilm and melting of a nanostructure at lower values of excitation laser light intensity.

Optical microscope for THG measurements

The nonlinear optical interaction of laser radiation with a single SHR nanostructure was investigated using an inverted microscope that was built based on a commercially available Nikon Eclipse microscope. In the custom-made microscope, we installed UV quartz lenses, aluminum mirrors, and mirror objectives. The radiation from the nanostructure was collected with a mirror objective (40 $\times$, NA = 0.5) and was analyzed with a CCD camera or a spectrometer equipped with a Hamamatsu CCD camera with the quantum efficiency higher than 20% in the UV range. In order to suppress the radiation at the fundamental frequency

after the objective, we used spectral filters. The second harmonic radiation was registered using a low pass filter with a cutoff wavelength of 600 nm. The third harmonic signals were registered using a bandpass filter with the central wavelength of 260 nm and transmission band of 60 nm. This specially designed microscope allows for optical measurements simultaneously in the near IR, visible, and UV spectral ranges from 220 nm to 950 nm.

Light transmittance through the SHR nanostructure

We measured the linear transmission spectra through a single SHR nanostructure (Fig.S2). We also calculated a plane monochromatic wave transmittance through the SHR nanostructure. As seen in Fig. 2, the measured and calculated transmittance (FDTD calculations) curves are almost identical and this confirms the validity of our theory.

Figure 2: Theoretical and experimentally measured light transmittance through the SHR nanostructure. The nanostructure parameters are as follows: the nanohole diameter is 700 nm; the nanorod dimensions are 350 nm×150 nm. The SHR nanostructure was made in a gold film with 200-nm thickness.

THG power curve

For a characterization of THG from a single SHR nanostructure we performed measurements of the dependence of the THG signal on the intensity of the excitation laser radiation (Fig.

S2). As it follows from the Figure that the THG can be approximated well by a power dependence with a coefficient $n = 3$. These measurements were performed with the nanostructure that realized the maximum THG signal. Parameters of the nanostructure are as follows: the nanohole diameter is 700 nm; the nanorod dimensions are 350 nm $\times$ 150 nm. The SHR nanostructure was prepared in a gold film with 200-nm thickness.

Figure 3: Dependence of the THG signal from a single SHR nanostructure on illumination intensity, fitted with a cubic power law.

Frequency mixing

As follows from Fig. 4c, the peak in the spectrum of the third harmonic generation with the central wavelength of 278 nm does not have a corresponding resonance at the fundamental frequency. We suggest that this resonant peak is caused by mixing of the ω_2 and ω_1 frequencies. This is evidenced by the following factors: (1) the wavelength of this resonance corresponds to the $(\omega_2 + 2\omega_1)$ frequency mixing: $\lambda = c/(\omega_2 + 2\omega_1) = 278 \text{ nm}$, where c is the speed of light; (2) in the third harmonic generation spectrum (Fig. 4c), the amplitude of the peak that corresponds to this resonance is considerably smaller than the amplitudes of remaining resonances (the frequency mixing process has a smaller cross section); and (3)

at the fundamental frequency, there is no plasmon resonance with the central wavelength $\lambda = 278 \text{ nm} \times 3 = 834 \text{ nm}$ (Fig. 4a). It should be stressed that the realization of $(\omega_2 + 2\omega_1)$ process is the consequence of coherent excitation of ω_1 and ω_2 plasmonic resonances by an ultra-short laser pulse with the duration of 6 fs.

Figure 4: Dependence of the resonant peak amplitude at mixed frequencies on time delay between laser pulse spectral components.

To confirm that the 278 resonant peak is a result of the frequency mixing process we present here the results of our additional measurements and calculations. We have realized in the experiment the situation when the two spectral components of the same laser pulse (that are responsible for an excitation of the resonant peak) are shifted on the time scale. This was done by using the chirped laser pulse technique. In these measurements the laser pulse intensity was the same as before. In the chirped pulse one spectral component of the pulse has higher group velocity and reaches a sample with the SHR nanostructure faster than the other spectral component of the same pulse. Thus, the spectral components corresponding to mixed frequencies will not reach the sample at the same time. The THG resonances are not sensitive to the laser pulse chirping (it was confirmed in our measurements), while the resonances at mixed frequencies should be sensitive to the pulse chirping. The use of the laser pulse chirping can give insight into the resonance nature at mixed frequencies.

Fig. S4 presents results of our measurements performed with the use of the chirping

pulse technique. The horizontal axis in Fig. 2 is a time delay between arrival to the sample of the laser pulse spectral components corresponding to the excitation of ω_1 and ω_2 plasmonic resonances of the SHR nanostructure. The decay of the resonant peak amplitude is the evidence of the mixed frequency nature of the peak and it is in good agreement with corresponding calculations of $(\omega_2+2\omega_1)$ process.

Figure 5: Spectral map of resonances at mixed frequencies.

Fig. S5 shows a spectral map of resonances at mixed frequencies for the measured and calculated THG signals. The resonant peak $(\omega_2+2\omega_1)$ correlates to the measured resonance peak at $\lambda=278$ nm. Other resonant peaks on mixed frequencies were not detected due to the following possible reasons: (1) they are weak because of the SHR nanostructure geometry, (2) they are very close to the strong $3\omega_1$, $3\omega_2$, $3\omega_3$ or $3\omega_4$ resonances.

Harmonics generation efficiency

In a separate experiment, we measured the harmonics generation efficiency. The average intensity of the excitation radiation was $I_\omega = 4.3 \times 10^5$ W/cm². The measured power of the second harmonic of radiation was $P_{2\omega} = 1 \times 10^{-12}$ W, while that of the third harmonic was $P_{3\omega} = 3 \times 10^{-10}$ W. Therefore, the cross section of the second harmonic generation by a single SHR nanostructure is $\sigma_{\omega \rightarrow 2\omega} = 2.4 \times 10^{-18}$ cm² = 2.4 Mb; for the third harmonic,

the generation cross section is $\sigma_{\omega \rightarrow 3\omega} = 7 \times 10^{-16} \text{ cm}^2 = 700 \text{ Mb}$. Our calculation of the near field distribution of an SHR nanostructure irradiated by a plane monochromatic wave with a wavelength of 260 nm shows that the near field is enhanced close to the end of the nanorod forming a region of $25 \times 50 \text{ nm}^2$ in size. Assuming that the experimentally measured radiation at the frequency of the third harmonic is emitted precisely from this region, we can estimate the average intensity of radiation of the third harmonic in this region, which was found to be $I_{3\omega} = 12 \text{ W/cm}^2$. In this case, the peak value of the power is $I_{3\omega, peak} = 3.4 \times 10^7 \text{ W/cm}^2$, and the amplitude of the radiation field at the frequency of the third harmonic constitutes a considerable part of the amplitude of the field at the fundamental frequency, $E_{3\omega} = 0.006 E_{\omega}$.

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