Second harmonic generation in hyperbolic metamaterials

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Abstract. The results of the synthesis, experimental studies, and numerical simulation of optical and nonlinear-optical properties of gold nanorods in porous anodic alumina templates are presented. Two features in the spectra of such structures in the vicinity of the wavelengths of 530 nm and 810 nm correspond to the epsilon-near-pole and epsilon-near-zero, respectively. Optical and nonlinear-optical properties of the structures in the spectral vicinity of these points are investigated. Experimentally observed features are consistent with the data of simulation.

1. Introduction

Hyperbolic metamaterials are composite artificial metal-dielectric nanostructured materials possessing the components of the permittivity and/or permeability tensor of opposite signs [1,2]. The key optical property of this class of the metamaterials is hyperbolic dispersion law, instead of elliptical dispersion in traditional materials. Moreover hyperbolic regime is directly related with two features of the spectra of the optical material’s properties. The first one is a change in the sign of the real part of one of the components of the effective permittivity tensor when passing it through zero (Epsilon Near Zero, ENZ). The second one is appearance of a pole of effective dielectric constant (Epsilon Near Pole, ENP) associated with high and strong dispersive dielectric constant in narrow spectral region [3]. The most popular designs of hyperbolic media include ordered array of metallic nanorods in a dielectric matrix or film consisting of alternating metal and dielectric layers. A plenty of unusual effects have been already experimentally discovered and theoretically explained in hyperbolic metamaterials, such as negative refraction [4], enhancement of spontaneous emission [5] and Raman scattering [6], transformation of the evanescent field of the object (radiated or scattered) into propagating mode in the far field [7]. Optics of hyperbolic media attracts great attention of researchers that is associated with the broad possibilities of their application in nanophotonics, biosensing [8], imaging [9], and waveguides [10].

Second harmonic generation (SHG) is a widely known technique sensitive for the properties of nanostructures. Forbidden in the media with inversion symmetry, the SHG originates from the surfaces and interfaces, where the symmetry is broken [11]. Moreover the nonlinear-optical response enhances under the resonance excitation that makes the method applicable for the study of metallic plasmonic nanostructures [12]. The increase in the SHG intensity under the phase matching conditions provides the efficiency of the SHG technique for investigations of the media with unusual dispersion
properties [13]. Thus, the study of the hyperbolic metamaterials by means of the nonlinear optical methods could discover fundamentally new effects, perspective for different applications [14]. At the same time, there is just a few experimental papers concerning the SHG in hyperbolic metamaterials [15].

In this paper complex experimental and numerical study of the optical and nonlinear-optical effects in arrays of gold nanorods in anodic alumina template is presented with the special accent on the ENZ and ENP spectral features.

2. Samples, experimental and simulation techniques

Arrays of metal nanorods were prepared by templated electrodeposition of gold into the pores of 50 μm thick anodic alumina films. To obtain alumina templates, two-step anodizing of high-purity aluminium (99.99%) in a 0.3 M H2SO4 solution at 25 V was used. According to the statistical analysis of the SEM images, the average distance between the centres of pores is 63 ± 5 nm, the pore diameter is 25 ± 5 nm, which corresponds to a porosity of about 14%. After the chemical dissolution of the remaining aluminium and the barrier oxide layer, 150 nm thick silver layer served as a current collector was formed on the bottom side of the alumina template by magnetron sputtering. The electrocrystallization of gold was carried out in a three-electrode electrochemical cell in the potentiostatic regime (E0 = −0.95 V) at room temperature from commercial electrolyte containing 0.05 M [Au(CN)2]−. The height of the rods was about 400 nm. Before carrying out optical measurements, the silver electrode was selectively dissolved in dilute HNO3 solution. A scheme of the obtained structures is shown in Fig. 1.

Optical properties of the composite are defined by two components ε⊥ and ε∥ of effective dielectric tensor that corresponds to perpendicular and parallel rods’ direction, respectively. To investigate linear optical properties of the metamaterial, transmittance of the composite film was measured. In experiment transmitted through the structure halogen lamp radiation was analyzed by a spectrometer. Because of the ENZ regime is governed by dielectric tensor component ε∥, the measurements of the spectra were performed for p-polarized fundamental beam. That allowed revealing the ENZ corresponding transition from elliptic to hyperbolic dispersion law.

Nonlinear-optical set-up was based on a femtosecond Ti-Sapphire laser system, with the pulse duration of 60 fs and repetition rate 80 MHz, operating in the wavelength range from 750 up to 880 nm. The p-polarized fundamental beam was focused on the sample into a spot of about 30 μm in diameter. Reflected SHG passed through a necessary set of color filters and was detected by a photomultiplier. In order to account for the fluctuations of the laser parameters, the reference SHG channel with a crystalline quartz as a nonlinear element was used, the measured SHG from the sample was normalized to that in the reference channel.

The spectra of the permittivity tensor components were calculated within the effective medium theory that includes the dipole-dipole interaction of the neighboring nanorods, accordingly [16]. Nonlinear-optical response was calculated, taking into account strong anisotropy of the medium, the distribution of the vectorial electric field within the structure and neglecting the spectral dependencies of the second-order susceptibility tensor components.

3. Results and discussion

Figure 2 represents the transmission wavelength-angular spectrum of the sample. It reveals two minima centred at approximately 530 nm and 810 nm and that are absent in the case of bulky gold or alumina. The first resonance is associated with the so called transverse localized plasmon resonance that corresponds to the electronic oscillations in the direction perpendicular to the long axis of nanorods [16]. This resonant feature turned out to be independent on the angle of incidence. Long-wavelength minimum is related to the collective longitudinal oscillations of the electronic gas in metal
nanorods. It vanishes for the normal incidence as there are no components of the fundamental field along the rods.

The spectrum of the SHG intensity, measured for the incident angle of 45°, is shown in Figure 3. The data demonstrate an enhancement of the quadratic signal more than two times in the spectral range centred at about 815-820 nm. It should be noted that in this spectral region the long-wavelength minimum for linear transmission was observed.

The real parts of the permittivity tensor components perpendicular and parallel to the long axis of the rods (ε⊥ and ε∥, respectively) were calculated in effective medium Maxwell-Garnett approach generalized to the case of an optically anisotropic system as described in [16], taking account of the morphology of Au/anodic alumina samples, i.e. the volume fraction of gold in the filled part of the template of about 14% and the length of the rods of about 400 nm. The obtained data are demonstrated in Figure 4. It can be clearly seen that at the wavelength of about 530 nm there is epsilon-near-pole point, where ε⊥ → ∞. ENZ feature, corresponding ε∥ → 0, is located near the wavelength 810 nm.

Figure 5 represents the calculated spectrum of the second harmonic intensity in the geometry corresponding to the experimental scheme, i.e. for the angle of incidence 45°, p-polarization of the fundamental and SHG radiation. The graph exhibits a strong amplification of the SHG response in the spectral vicinity of the wavelength of 810 nm. The origin of SHG enhancement is increasing of electric field in the structure caused by extremely small ε∥ and continuity of normal component of electric displacement field.
\( Re(\varepsilon_{||}) \) – red line, \( Re(\varepsilon_{\perp}) \) - black line. intensity. Angle of incidence is 45°.

Comparison of the obtained data allows one to conclude that the two features in transmission spectra at about 530 nm and 810 nm are associated with ENP and ENZ points, respectively. Thus, the hyperbolic dispersion regime is realized at the wavelengths above 810 nm. The SHG response is strongly enhanced in the spectral vicinity of the ENZ point that can be attributed to the local field amplification owing to the longitudinal plasmon resonance excitation. SHG experimental data stay in a good agreement with the results of numerical simulations. Small differences between them can be caused by some inaccuracies of effective medium approach and the fact that the permittivity of the bulk gold was taken for the simulation, whereas it can slightly differ from the corresponding value for electrodeposited metal.

4. Conclusion
Optical and nonlinear-optical properties of the array of gold nanorods in porous anodic alumina matrix were studied experimentally and numerically. Epsilon-near-pole and epsilon-near-zero points were detected as minima in transmission spectrum. Strong enhancement of the SHG signal was detected in the spectral vicinity of the epsilon-near-zero point owing to the local field enhancement within the structure.

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