Experimental study of nonlinear absorption in hyperbolic metamaterials based on ordered arrays of nanorods

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Abstract. Nanophotonics is a rapidly developing branch of physics that studies light interaction with nanoscaled objects such as metamaterials. Hyperbolic metamaterials (HMMs) based on ordered arrays of metal nanorods embedded in a dielectric matrix are of great interest due to their nontrivial optical properties and abilities to control over the parameters of light. In this article, we present the results of nonlinear absorption measurements in HMMs based on ordered arrays of silver nanorods. The main finding consists in the spectral vicinity of Epsilon-Near-Zero and Epsilon-Near-Pole features.

1. Introduction

Hyperbolic metamaterials (HMMs) are highly anisotropic artificial media, where the main components of the permittivity tensor are of the opposite signs. HMMs attracted considerable attention recently because of their appealing optical and nonlinear-optical properties caused by unique dispersion law unattainable in natural media \cite{1, 2}. Special dispersion of HMMs possesses two spectral features of the effective permittivity: zero-crossing point (Epsilon-Near-Zero, ENZ) $\varepsilon_\parallel = 0$ and a pole (Epsilon-Near-Pole, ENP) $\varepsilon_\perp \rightarrow \infty$, where $\varepsilon_\parallel, \varepsilon_\perp$ are the components of effective permittivity tensor perpendicular and parallel to the long axes of the nanorods. The regions where $\varepsilon_\parallel, \varepsilon_\perp < 0$ are characterized by hyperbolic dispersion giving a name to the material class \cite{3}. One of HMMs’ common designs represents arrays of metal nanorods embedded in a dielectric template. In the case of nonmagnetic material $\mu = 1$, isofrequency surface for the TM mode of light is described as:

$$\frac{k_x^2 + k_y^2}{\varepsilon_\parallel} + \frac{k_z^2}{\varepsilon_\perp} = \frac{\omega^2}{c^2} \quad (1)$$

where $k_x,y,z$ are the components of the wave vector, $\omega$ is the frequency of the electromagnetic wave and $c$ is the speed of light, Oz is the optical axis \cite{1}.

Light interaction with HMMs composed of metal nanorods in a dielectric matrix leads to the excitation of transversal and longitudinal surface plasmon resonances appearing as two minima in the transmission spectra. The longitudinal one can be excited only in the p-polarized incident beam at oblique incidence. Spectral positions of resonances correspond to ENP and ENZ, respectively \cite{4}. It is known that zero-crossing point of the $\text{Re}\varepsilon_\parallel$ drastically changes the light-matter interaction through transition from elliptical to hyperbolic dispersion, whereas the pole brings about the localization of the electromagnetic

\cite{1, 2, 3, 4}
field. Various linear and nonlinear-optical effects have been observed in the spectral vicinities of ENZ and ENP features, such as the negative refraction of light [5], transformation of the evanescent field of an object into propagating mode [6], giant optical birefringence [1], and enhancement of such nonlinear effects as second [7] and third harmonic generation [3].

The change of the complex nonlinear refractive index can be produced by the powerful incident beam. It leads to modification of light propagation and appearance of third-order nonlinear effects such as self-focusing and two-photon absorption. An increase in the nonlinear absorption $\beta$ has been associated with the continuity of the normal component of the electric displacement field in the vicinity of $Re(\varepsilon) \to 0$ and consequent with the increase in the electric field within the structure. The enhancement of the nonlinear-optical response occurs as well in metamaterials at the zero-crossing point of the effective permittivity [10]. The nonlinear refractive index and nonlinear absorption have been meticulously studied theoretically in the hyperbolic dispersion regime, providing positive nonlinearity at elliptic regime and negative nonlinearity at hyperbolic regime [11]. At the same time, there have been no thorough experimental studies of the effect in a wide spectral range.

In this paper, experimental studies of the nonlinear absorption by means of z-scan technique in silver nanorods-based HMM are presented. Spectroscopy of the nonlinear absorption reveals the features, associated with the ENZ and ENP points.

2. Experiment

Arrays of silver nanorods were prepared by templated electrodeposition of Ag inside the pores of anodic aluminum oxide (AAO). The AAO templates were obtained by anodization of high purity aluminum in 0.3 M selenic acid electrolyte at 48 V. According to scanning electron microscopy (SEM) images, the diameter of nanorods and the distance between their centers were $D_p = (41 \pm 9)$ nm and $D_{int} = (105 \pm 14)$ nm, respectively. Thus the volume fraction of silver in the filled part of the template is about 14%. The average length of the nanorods was found to be 700 nm.

Figure 1. (a) HMM transmission spectra recorded at the angles of incidence $0^\circ$, $10^\circ$, $20^\circ$, and $30^\circ$; (b) calculated spectra of real and imaginary parts of the permittivity components with $\lambda_{ENP} = 400$ nm and $\lambda_{ENZ} = 750$ nm, hyperbolic dispersion regime is realized at $\lambda > 750$ nm (colored blue); (c) calculated wavelength-angular spectrum of p-polarized beam refractive index.

Transmission spectra of the arrays of Ag nanorods in AAO matrix measured for the p-polarized incident beam demonstrate two minima centered at $\lambda = 400$ nm and $\lambda = 750$ nm corresponding to the transversal and longitudinal resonances, respectively. It can be seen that the most efficient excitation of longitudinal resonance occurs for $\theta > 20^\circ$ (Fig.1 (a)).
Permittivity components were calculated within the effective medium model as:

$$\varepsilon_\perp = \frac{(1 + \rho)\varepsilon_m\varepsilon_d + (1 - \rho)\varepsilon_d^2}{(1 + \rho)\varepsilon_d + (1 - \rho)\varepsilon_m}, \varepsilon_\parallel = \rho\varepsilon_m + (1 - \rho)\varepsilon_d$$

(2)

where $\rho$ is volume fraction of silver, $\varepsilon_m$, $\varepsilon_d$ are dielectric functions of Ag and AAO [1]. Simulations, performed using $D_p = 35$ nm and $D_{out} = 105$ nm, demonstrate the spectral positions of the ENZ at $\lambda = 750$ nm and of the ENP at $\lambda = 400$ nm (Fig.1 (b)), so the hyperbolic dispersion is achieved at $\lambda > 750$ nm.

Wavelength-angular spectrum of the imaginary part of the refractive index was calculated for the p-polarized beam as $n = \sqrt{\varepsilon_\perp + \sin^2 \theta (1 - \varepsilon_\parallel/\varepsilon_\parallel)}$, where $\theta$ is an incident angle [1]. In (Fig.1 (c)) one can observe a narrow increase in $Im(n)$ near ENZ and a smaller enhancement near ENP. These regions of high absorption are associated with plasmon resonances excitation. The difference in widths of the minima in the experimental transmission spectrum and calculations is associated with slightly different length of nanorods.

Z-scan technique was used for the studies of the nonlinear absorption of the HMMs near the transition from elliptical to hyperbolic dispersion law [12]. As the fundamental radiation, the p-polarized output of a Ti:Sa laser with tunable wavelength $730 \pm 900$ nm was used, with the FWHM of the spectral line of about 10 nm, the pulse duration of 50 fs, the repetition rate of 80 MHz, and the average power of 80 mW. The incident beam with the diameter of $D = 3$ mm was focused by a simple positive-meniscus lens with the focal length of $F = 5$ cm. The sample was moved in the vicinity of the lens focal plane, thus the fundamental beam intensity irradiating the HMM was varied. The radiation at the pump wavelength was spectrally selected by color filters and detected by a photodiode (Fig. 2 (a)), so the influence of luminescence on the data is excluded. The dependence of transmission on the $z$-coordinate was measured, $T(z)$, where $z = 0$ corresponds to the lens focal plane. The Rayleigh length is determined as $z_0 = n_0\pi w_0^2/\lambda$, where $n_0$ is the air refractive index, $w_0 = 2\lambda F/D$ is the radius of the Gaussian beam in the lens focal plane. In our experiments, for example, for $\lambda = 790$ nm $z_0 \approx 3$ mm and $w_0 \approx 30$ $\mu$m.

3. Results and discussion

Typical z-scan patterns are presented in Fig. 2(b). In the spectral region with elliptic dispersion ($\lambda = 730$ nm, blue points) a gap of normalized transmission near the focus is observed, whereas in the hyperbolic dispersion range ($\lambda = 810$ nm, red points) there is a maximum of the transmitted intensity near the point $z=0$. The analysis $T(z)$ data obtained for various wavelengths indicated that two photon absorption occurred at $\lambda < 800$ nm and saturation of absorption at $\lambda > 800$ nm.

As the obtained data $T(z)$ for all the wavelengths were well approximated by the Lorentz function with FWHM equal to $2z_0$, so the influence of higher-order nonlinear effects was excluded. The amplitude of the peaks or gaps $A$ was obtained after the approximation. The nonlinear absorption is determined as $\beta = 2\sqrt{2A}/(w_0L_{eff}l_0)$, where $L_{eff} = 4\pi\lambda (1 - \exp^{-4\pi Im(n)L/\lambda})/Im(n)$ is the effective length, $l_0$ is the laser intensity, $L$ is the thickness of the sample, i.e. the length of nanorods.

The spectrum of $\beta$ for p-polarized light at $\theta = 30^\circ$ calculated from these approximation data is shown in Fig. 2 (c). One can see the change of the sign of $\beta$ near $\lambda = 800$ nm. This modulation is associated solely with HMM, as the empty AAO template possesses no specific features in the spectral range under study. Also no effect was observed for the s-polarized incident beam.

The HMMs nonlinear response for the fixed incident angle is determined by:

$$\beta \propto Im \left( \frac{\chi^{(3)}_{xxzz}}{\varepsilon_\perp} + \frac{\chi^{(3)}_{zzzz}}{\varepsilon_\parallel} \right)$$

(3)

where $\chi^{(3)}_{xxzz,zzzz}$ are the third-order susceptibility tensor components, xOz is the incident plane [11]. As seen from equation (3), the linear anisotropy of the metamaterial can strongly enhance the nonlinear
response, particularly when the linear permittivity tensor components become small, as in the case of the ENZ regime. Near the ENZ the second term of Eq. 3 has a singularity, while $Re(\varepsilon_{||})$ tends to zero (Fig. 1 (b)). As the contribution of first term is determined by $\varepsilon_{\perp}$ that is nearly constant in this spectral region, the $\varepsilon_{||}$ sign-change produces the sign-change of $\beta$ near the ENZ point. The sharp increase in $\beta$ observed in the spectral vicinity of $\lambda = 2\lambda_{ENP} = 800$ nm can be also associated with the two-photon transversal plasmon excitation in the HMM under study.

4. Conclusion
Summing up, nonlinear absorption in HMMs based on ordered arrays of Ag nanorods in AAO template was studied experimentally in the spectral vicinity of the ENZ and ENP spectral points. A significant enhancement of $\beta$ along with its sign reversal in the hyperbolic dispersion regime was observed. This effect is associated with the transition between elliptic and hyperbolic dispersion and two-photon excitation of transversal plasmon resonance.

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