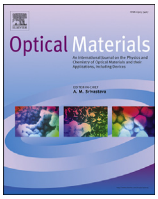
Optical Materials 60 (2016) 552–558

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Active control of highly efficient third-harmonic generation in ultrathin nonlinear metasurfaces

Zibo Gong [a, 1], Chong Li [a, 1], Xiaoyong Hu [a, b, *], Hong Yang [a, b], Qihuang Gong [a, b]

[a] State Key Laboratory for Mesoscopic Physics & Department of Physics, Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, People's Republic of China
[b] Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China

ARTICLE INFO

Article history:
Received 2 July 2016
Received in revised form
1 August 2016
Accepted 9 September 2016

Keywords:
Metamaterial-induced transparency
Third harmonic generation
Nanocomposite

ABSTRACT

Active electric control of highly efficient third harmonic generation was realized in an ultrathin nonlinear metasurface by using a nanocomposite consisting of gold nanoparticles dispersed in polycrystalline strontium titanate as the electro-optic material. Owing to the nonlinearity enhancement associated with the slow light effect, quantum confinement effect, and field-reinforcement, a high conversion efficiency of 3×10^{-5} was obtained, which is two orders of magnitude larger than previously reported efficiencies at comparable pump intensities. A modulation of 12% in the intensity of the third harmonic generation and a 30-nm shift in the transparency window center were achieved by varying the applied voltage from −30 V to zero. Our results pave the way toward the realization of multi-functional integrated photonic devices and chips based on metasurfaces.

1. Introduction

Third harmonic generation (THG), a kind of third-order nonlinear optical phenomenon, is not only an indispensable technology widely used in the fields of tunable laser frequency conversion [1] and high-energy coherent light sources [2,3], but also a feasible approach for realizing various integrated photonic devices, such as bio-imaging devices [4–7], drug delivery devices [8], and photovoltaic devices [9]. In the quantum picture, three identical photons with an energy of ω interact with a nonlinear material, thereby producing a new photon with an energy of 3ω. However, the third-order nonlinear optical response of conventional materials is intrinsically weak, and thus a long interaction length or high incident intensity is needed for efficient THG [10]. For macroscopic photonic structures, phase matching technology is an effective way to enhance THG. Moreover, confining light in optical resonators could be used to improve the incident intensity, thereby enhancing THG [10,11]. However, metasurfaces are ultrathin, such that the interaction length between light and matter is much smaller than the wavelength of the incident light; this means that phase matching conditions cannot be exploited when using metasurfaces [12,13]. The plasmonic modes provided by meta-molecules possess the unique ability of confining light into sub-wavelength scale structures, which contributes to the nonlinearity enhancement of metasurfaces [14–17]. Up to now, the conversion efficiency of THG has only reached 10^{-7} with a peak pump intensity of about 300 MW/cm^2 (or 10^{-6} with a peak pump intensity of several GW/cm^2) in metamaterials [18–24]. An active control of THG could lead to important applications in ultrahigh-speed and ultrawide-band information processing chips. Active control of THG with a high conversion efficiency has not yet been realized, which has restricted the practical applications of metasurface in integrated photonic devices.

2. Material and methods

Here we report the realization of active electrical control of high efficient THG in an ultrathin metasurface, which consisted of an array of square lattices of meta-molecules with a thickness of 50 nm deposited on the upper surface of a 150-nm-thick nanocomposite layer with a strong linear electro-optic effect. Both external and intrinsic nonlinearity enhancement was used in our experiment. The former was achieved by using the metasurface, while the latter one was realized in the nanocomposite film. The

---

[*] Corresponding author. State Key Laboratory for Mesoscopic Physics & Department of Physics, Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, People's Republic of China.
E-mail address: xiaoyonghu@pku.edu.cn (X. Hu).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.optmat.2016.09.029
0925-3467/© 2016 Elsevier B.V. All rights reserved.

meta-molecule in our metasurface consisted of a subradiant and a superradiant meta-atom. First, owing to the destructive interference between the subradiant and superradiant plasmonic modes provided by the meta-molecules, a transparency window was obtained in the transmission forbidden band of the metasurface sample. Scalora et al. and Xu et al. noted that there is a remarkable slow-light effect around a metamaterial-induced transparency window, which contributes to the external nonlinearity enhancement of the metasurface sample, thus extending the interaction time between photons and material [16,17]. Additionally, the light reinforcement effect of the plasmonic modes provided by the meta-molecules also contributes to the nonlinearity enhancement of metasurface samples [14,15]. These factors above both contribute to the external nonlinearity enhancement of the metasurface sample. Here, the nanocomposite material was composed of gold nanoparticles dispersed in polycrystalline strontium titanate (nano-Au:polycrystalline-$SrTiO_3$). SrTiO3 has both impressive third-order optical nonlinearity and excellent electro-optic properties [25]. The strong quantum confinement effect provided by the gold nanoparticles and nanoscale grains of polycrystalline $SrTiO_3$ contribute greatly to the third-order optical nonlinearity enhancement of the nanocomposite nano-Au:polycrystalline-$SrTiO_3$ [26–30]. Au nanoparticles can also inject hot-electrons into the SrTiO3 nanocrystals, so that the carrier density is increased to enhance the nonlinearity of the nanocrystallites [31]. Further, Fischer et al. also pointed out that the electric-field amplitude of an incident pump laser beam was nonuniformly distributed between the two constituents of the nanocomposite [32]. These factors also contribute to the intrinsic nonlinearity enhancement of the metasurface sample. A THG conversion efficiency as high as 4×10^{-5} was obtained in our experiment, which is one order of magnitude higher compared with values in previous reports [18–24]. Markovin et al. pointed out that $SrTiO_3$ has an excellent electro-optic effect, which results in an external voltage induced refractive index change [33]. In this study, a modulation depth of 12% in the THG intensity was achieved when the applied voltage was changed from −30 V to 0 V. This paves the way for the realization of multi-functional integrated photonic devices based on metasurfaces.

A nano-Au:polycrystalline-$SrTiO_3$ nanocomposite film with a thickness of 150 nm was deposited on the surface of a 400-nm-thick silicon dioxide (SiO_2) layer on a silicon substrate by using a laser molecular beam epitaxy growth system (Model LMBE450, SKY Company, China) [34]. The doping concentration of gold nanoparticles, with an average diameter of 25 nm, was about 10%. An atomic force microscopy (AFM) image of a 150-nm-thick nanocomposite film is shown in Fig. 1(a), which indicates that the average surface roughness was less than 6 nm and the diameters of these SrTiO3 crystallites were under 10 nm. The crystallites being on the nano-scale ensured the quantum confinement effect [26–28]. An electron-beam lithography system (Model Raith 150, Raith Company, Germany) was used to prepare the periodic patterns of the square lattice of the meta-molecules. The lattice constant was 680 nm, as shown in Fig. 1(d) and (d). The patterned area was about 200 μm × 200 μm. A single meta-molecule was formed by a single long gold nano-cuboid, acting as the superradiant meta-atom, and a pair of short gold nano-cuboids, acting as the subradiant meta-atom, as shown in Fig. 1(e). The length, width, and height were 230, 60, and 50 nm for the long gold nano-cuboid, and 215, 60, and 50 nm for the short gold nano-cuboid. The distance between the long and short gold nano-cuboids was 50 nm in the Y-direction. The distance between the two short gold nano-cuboids was 85 nm in the X-direction. Additionally, Si and SiO2 were chosen as substrate materials, as they are standard substrates for on chip integration and are CMOS compatible, which may be relevant for future applications.

3. Experimental

To confirm the intrinsic nonlinearity enhancement, we measured the nonlinear refractive index n_2 of an Au:nanocrystal-$SrTiO_3$ film at 1400 nm using the close-aperture Z-scan method with a 35-fs, 1400-nm laser. The measured close-aperture Z scan curve is shown in Fig. 1(b). The normalized transmission can be fitted to [35].

$$T(z) = 1 + \frac{4\Delta\varphi x}{(x^2+9)(x^2+1)}, \tag{1}$$

where T is the normal transmittance, $x/z = z_0$, z is the longitudinal distance from the focal point, z_0 is the Rayleigh range of the laser beam, and $\Delta\varphi$ is the phase change. The nonlinear refractive index n_2 could be obtain from Ref. [35].

$$n_2 = \frac{\Delta\varphi\lambda\alpha}{2\pi I_0\left(1 - e^{-\alpha L}\right)}, \tag{2}$$

where λ is the laser wavelength in vacuum, α is the linear absorption index, I_0 is the peak intensity of the laser beam, and L is the sample thickness. The non-linear refractive index was measured to -1.6×10^{-10} *esu*, which is two orders larger than for the bulk single-crystal of $SrTiO_3$ ($n_2 = -26.7 \times 10^{-13}$ *esu*. [25]).

To study the linear transmission properties of the metasurface sample, we adopted a micro-spectroscopy measurement system to measure the linear transmission spectrum of the metasurface sample. A normally incident beam from a super-continuum light source was focused on the upper surface of the metasurface sample with a spot size of about 150 μm. A polarizer and a wave plate were used to control the polarization state of the incident light. The output signal propagating through the metasurface sample was detected by a fiber monochromator (Model NIR 512, Ocean Optics, USA). The polarization state of the incident light was set to be transverse-magnetic (TM) polarized and the electric-field vector of the incident light was set to be parallel to the long nano-rod, i.e., along the X-axis direction. The measured linear transmission was normalized with respect to a reference sample without the patterned area, i.e., the reference structure was: Si substrate/400-nm-thick SiO_2 layer/150-nm-thick nanocomposite layer.

The experimental setup used to study the THG in the metasurface is shown in Fig. 2(a). A beam (with a pulse duration of 35 fs and a repetition rate of 1 kHz) from a femtosecond optical parameter amplifier system (model Opera Solo, Coherent Company, USA) propagated through an attenuator and a dichroic mirror before being focused into a spot with a size of about 150 μm by using a high N.A. objective lens (Mitutoyo 100×, NA = 0.7); the beam was normally incident on the upper surface of the metasurface sample. The THG signal was collected by the same objective lens (N.A. = 0.7) and reflected by the dichroic mirror, then detected using a fiber monochromator (model HR 4000, Ocean Optics, USA) with a resolution of 0.74 nm. The light signal transmitted through the metasurface sample was collected by another objective lens and detected using an infrared CCD, which helped to adjust the position of the incident light spot. We measured the THG signal when the metasurface sample was excited by TM-polarized incident light at different wavelengths with a peak intensity of 170 MW/cm^2. As reference, we also measured the THG signal when the sample was excited by TE-polarized light. Further, a sample with no meta-molecule arrays was excited with TM-polarized light as a reference. Furthermore, the THG conversion efficiency was measured based on the method used by Yang et al. [10]. First, we used a light beam with a known power to calibrate the fiber spectrometer, aiming to measure the relationship between the counts response