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Progressive Self-boosting Anapole-enhanced Deep-ultraviolet Third Harmonic during Few-cycle Laser Radiation

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Abstract

Nanoantennas made of high-index semiconductors with a strong nonlinearity and supported optical Mie-type resonances offer a promising alternative platform for nonlinear nanophotonics. In this letter, we employ an array of amorphous silicon nanodisks with varying diameters to produce a broadband deep-ultraviolet third harmonic of a few-cycle Ti:sapphire oscillator. Ultrashort light pulses efficiently deposit their energy at the center of the disks where the electric field is strongly amplified by the anapole states. This leads to a progressive material modification in an extreme multishot ($>10^{10}$ pulses) and a rather low fluence ($<10^{-3}$ J/cm²) regime, drastically differing from other known mechanisms such as nonthermal plasma annealing or thermal melting-induced recrystallization. We attribute the material modification to femtosecond laser-induced excitation of dangling bonds, which leads to a gradual boosting of the third harmonic conversion efficiency and broadening of its spectral bandwidth.

KEYWORDS: anapole mode, third harmonic generation, deep-ultraviolet, silicon photonics, few-cycle laser, ultrafast nonlinear optics, all-dielectric nanoantennas

One of the most studied effects in the field of nonlinear optics is coherent phase-matched optical frequency upconversion.¹ Recently, the dramatic advancements of nanofabrication and optical near-field probing techniques have led to a gradual shift of research interest from phase-matched optical interactions to non-phase-matched processes occurring at a deeply subwavelength scale.²⁻⁴ Nonlinear optics at the nanoscale has become one of the major success stories of modern optics, which hold great potentials for a host of applications such as nanolasers, optical bio-labels, -imaging and -sensing, optoelectronic hybrid devices, etc.⁵⁻⁸ In particular, it was recently shown that optical up- and down-conversion on the nanoscale is possible.⁸⁻¹⁶ Boosting the efficiency of frequency conversion in nanodevices is a subject of extensive theoretical and experimental investigations. Plasmonics, another field of light-matter interaction at nanoscale, provides a platform to enhance the nonlinear optical effects due to the fact, that metallic nanostructures at plasmon resonances are capable of focusing the excitation field far beyond the diffraction limit and thus significantly enhancing the electric near-field strength.^{10,17,18} However, the plasmonic nanoantennas solely enhance the

electric field in vicinity of the metal surface.¹⁰ This strongly limits the nonlinear processes that emerge from a bulk response such as third harmonic generation (THG).⁹ Furthermore, the plasmonic nanostructures suffer from strong Ohmic losses in the ultraviolet, visible and near-infrared spectral region and thus exhibit low thermal damage threshold.^{19–21}

Recently, due to their efficient ability of confining and manipulating light at the subwavelength scale via Mie-type resonances, nanoantennas made of high-index semiconductors^{22–25} with a strong nonlinearity offer a promising alternative platform for nonlinear nanophotonics.^{3,26–29} It has been demonstrated that resonantly excited crystalline silicon nanoparticles fabricated by an optimized laser printing technique³⁰ can exhibit strong second-harmonic generation (SHG) effects attributed to a polycrystalline structure of nanoparticles.³¹ Harmonics generation effects affected by magnetic dipole resonance of single dielectric nanodisks,^{11,12} or by more complex Fano-resonant dielectric metasurfaces^{32–35} have been recently studied. Significant enhancement of THG has been demonstrated in thin Si, Ge, and TiO₂ nanodisks and hybrid metasurfaces through the excitation of anapole state.^{13–15,36} This is a nonradiative state that arises due to the destructive interference between the fields generated by a toroidal dipole and an electric dipole induced in a scatterer by incident waves and accompanied by increasing electromagnetic energy inside the scatterer.^{37–39} During last five years the physics of anapole states spurs considerable research interest to the conditions of their excitations and their different properties. From the application point of view, the investigations of anapole states result in new achievements in fields of energy storage, sensing, lasing, metamaterials, and nonlinear optics. Comprehensive discussions of important historical and physical aspects of the anapole optics are presented in recent reviews of several groups.^{40–42} Note, excitation of anapole states does not lead to storage of energy at large timescale in the nanostructure, in contrast to the embedded modes.⁴³

Unlike their plasmonic counterparts, the semiconductor-based nanoantennas have much higher internal electric and magnetic fields^{30,44} and much lower inherent absorption and thus weaker thermal effects. However, when focusing a few-cycle intense laser pulse into a solid,

a substantial amount of electrons will be suddenly populated to excited states, forming a transient nonequilibrium plasma.⁴⁵ This can introduce some nonthermal responses of the solid materials such as Coulomb explosion,⁴⁶ lattice instability and disorder⁴⁷ or plasma annealing.⁴⁸ Considering that the anapole state exhibits maximized storage of electromagnetic energy inside a particle, it remains largely unexplored how the nonthermal processes will influence the nonlinear responses of semiconductor nanoantennas under the illumination of ultrashort pulses with high peak intensity.

In this letter, we demonstrate that a few-cycle, low fluence, and high repetition rate laser can surprisingly improve the nonlinear response of amorphous silicon nanodisks at anapole state. As a result, the anapole state-enhanced THG intensity is progressively self-boosted during the laser irradiation. Upon this self-boosting effect, we produce a broadband, high repetition rate, coherent, and miniature light source in the deep-ultraviolet spectral region. From the standpoint of practical applications, such a deep-ultraviolet source is highly desirable in the research fields of ultrafast spectroscopy and photoemission electron microscopy.

Our previous works have demonstrated that a high-refractive index nanodisk with a high diameter (D)-to-thickness (t) (c.f., Fig. 1a) aspect ratio exhibits anapole states.^{37,39} In order to match our Ti:sapphire laser that is centred at near 820 nm, we design a silicon-on-silica nanodisk with $D=660$ nm and $t=80$ nm. Finite element method (FEM)-based numerical simulations indicate that the anapole state manifests itself as a decrease of normal component of the near-field $|E_z|$ (c.f., blue curve in Fig. 1d) while a strong increase of electric field intensity inside the disk (c.f., Fig. 1b,c and red curve in Fig. 1d). Here we utilize the second-order anapole state, which provides the highest field enhancement inside the disk.³⁹ However, the resonant spectrum of a single silicon disk does not cover the ultrabroad bandwidth of a typical few-cycle Ti:sapphire oscillator (inset in Fig. 1d). As predicted by the numerical simulations in Fig. 2a, the resonant wavelength of the anapole state monotonically redshifts with the increase of the disk's diameter.¹³ Therefore, we fabricated an array of silicon disks

with diameters ranging from 470 to 970 nm, as shown in Fig. 2b. The corresponding resonant wavelengths (open circles in Fig. 2a) span the entire spectral range of our laser. As a result, compared to the THG radiation from the glass substrate (filled area in Fig. 2c), our silicon disks produce an even broader bandwidth of THG in the deep-ultraviolet spectral region (red curve in Fig. 2c), increasing from 24 to 30 nm. Furthermore, the spectrum of harmonic emission from the silicon disks slightly redshifts with respect to that emission from the substrate. This is due to the fact that the bigger the disk, the higher the intensity enhancement as well as larger active volume, leading to a higher total harmonic conversion efficiency at longer wavelengths, as depicted in Fig. 2d.

Interestingly, we find that the THG emission from the silicon disks rapidly grows over time (c.f., red curve in Fig. 3a). The laser peak intensity is estimated to be ~ 0.1 TW/cm². We fit the experimental curve by a saturating function of $a \cdot b \cdot \exp(-k \cdot t)$ (black curve), where k denotes the growth rate. When stretching the pulse duration from 7.6 fs to 9.5 fs while keeping the same laser averaged power (green curve in Fig. 3a), the growth rate of THG becomes noticeably lower, reducing from 1.49 to 0.62 min⁻¹. This implies that the observed progressive increase of THG is related to the pump peak intensity rather than the fluence. Furthermore, as plotted in Fig. 3b, the growth rate of THG as a function of the incident laser intensity I_0 suggests that our observation is caused by a highly nonlinear process.

The progressive increase of harmonic intensity is highly reproducible. The signal always features an gradual increase upon a sudden translation to a new array, as indicated by the dashed arrows in Fig. 3a (at $t=3$ min for 7.6 fs pulse and at $t=4.5$ min for 9.5 fs case). During the measurement with the 9.5 fs pulse, we insert a BK7 glass (at $t=3$ min as marked by the solid arrow in Fig. 3a) in front of our ultraviolet detector, which acts as a longpass filter. We confirm thereby that the enhanced signal indeed arises from the ultraviolet THG signal rather than the scattering of fundamental photons. Furthermore, we turn the laser beam off when the signal has nearly saturated (see Fig. 3c), waiting for 8 min and turn it on again. The THG signal restarts at the value it has before switching off the laser (at $t=3$

min). This suggests that the silicon disks have been irreversibly modified by the laser. As a next step, we perform a long term exposure of a new sample. As shown in Fig. 3d, the signal abruptly increases at the beginning ~ 5 min and nearly saturates afterwards up to 160 min. The experimental curve (gray curve) nicely fits the aforementioned function $a \cdot b \cdot \exp(-k \cdot t)$ (red curve). As shown in Fig. 3e, it should be pointed out that at the peak intensity of 0.1 TW/cm^2 , we do not observe the growth of THG emission from a bare silicon film with the same thickness (80 nm).

In Figure 4a, we compare the spectra of THG radiated from a pristine disks array (dashed black curve) and an exposed one (solid black curve). We employ a very low laser power to carry out these measurement to ensure that the THG signal does not vary during the experiments. We observe that not only the harmonic intensity has been enhanced by the ultrashort laser irradiation, but also the spectral bandwidth has been further broadened from 30 nm to 34 nm towards short wavelength. The spectrally resolved THG enhancement factor (dashed dotted curve) peaks at $\lambda_1 \sim 250$ nm, and another local maximum appears at $\lambda_2 \sim 273$ nm. As previously indicated in Fig. 2c, the spectrum of THG emission from the glass substrate also exhibits two local maxima at the same wavelength, indicating that the fundamental laser has two local peak field strength at $3\lambda_1 \sim 750$ nm and $3\lambda_2 \sim 819$ nm, respectively. In contrast to the spectral harmonic enhancement factor, the fundamental electric field at $3\lambda_1$ is weaker than that at $3\lambda_2$. This implies that the laser illumination at short wavelengths results in a stronger material modification. The intensity of THG emission from the pristine silicon disks is independent of laser polarization θ (c.f., red circles in Fig. 4b). Here $\theta=0$ degree denotes that laser is polarized along x -axis. However, after laser-induced material modification, THG versus θ follows $\cos^2(\theta)$ (blue curve in Fig. 4b). This is attributed to that the laser intensity enhancement and thus the material modification inside the silicon disks exhibits an asymmetric spatial distribution along θ .

The TH signal radiated from the silicon disks is directly related to the third order non-linear polarization $P^3 \propto \chi^{(3)}(gE_0)^3$ of the silicon atoms, where $\chi^{(3)}$, g , and E_0 denote the

third order nonlinear susceptibility, near-field enhancement factor, and the incident fundamental laser field strength, respectively. Therefore, the progressive growth of THG by the laser irradiation may be attributed to two possible reasons: either 1) the field enhancement factor or 2) the nonlinear susceptibility are enhanced by the laser-induced material or geometrical modification. Indeed, if our amorphous silicon disks are recrystallized through the laser-triggered thermal or plasma annealing, the near-field enhancement factor can be further increased, because the crystalline silicon has a lower optical absorption loss with respect to the amorphous one.⁴⁹ However, our applied laser fluence ($\sim 0.001 \text{ J/cm}^2$) is nearly 240 times lower than the threshold ($\sim 0.24 \text{ J/cm}^2$) for thermal crystallization of amorphous silicon nanoparticle,³⁰ and ~ 100 times weaker than the threshold ($\sim 0.1 \text{ J/cm}^2$) for plasma annealing-induced nonthermal crystallization.⁴⁸ The anapole-enhanced intensity inside the disks remains much lower than these two thresholds taking into account that the enhancement factor is < 10 as shown in Fig. 1c. Furthermore, we confirm that the size and geometry of our silicon disks are not changed after long term laser exposure by high resolution SEM imaging, as displayed in Fig. 4c. Consequently, we conclude that the self-boosting of THG is not caused by the further enhancement of near-field intensity by laser-induced material or geometrical modification.

Considering that our results are observed in a regime of rather low laser fluence and extremely large number of laser shots (10^{10}), we believe that our observation is closely related to the mechanism that was first reported by Kwak *et al.*⁵⁰ In this mechanism, the exposure of a semiconductor by a fs laser with extremely high repetition rate can result in an excitation of the dangling bonds. In ref. 50, the excitation of dangling bonds induces lattice instability and disorder, therefore, the second harmonic generation progressively decreases over time. In contrast, in our case, the dangling bonds can enhance the third order nonlinear susceptibility, because, according to the nonlinear anharmonic model, the looser bound of a valance electron by the nuclear, the higher nonlinear susceptibility.⁵¹ Figure 4d and e display the optical microscopy images of our silicon disks without and with laser irradiation,

respectively. We observe a clear change of silicon colour from yellow to green. This offers an indirect evidence of excitation of dangling bonds, as the dangling bonds have a strong absorption in the near-infrared spectral range.⁴⁹ The dangling bonds at the surface of silicon disks can be easily passivated through oxidation. However, the anapole state mainly amplifies the laser intensity at the center of the disks (Fig. 1b,c), and thus no recovery of THG is observed in the absence of laser fluence over 8 min.

In summary, we have demonstrated the utilization of amorphous silicon disks that are excited at second-order anapole state to produce broadband deep-ultraviolet THG of a few-cycle Ti:sapphire oscillator. Compared to our previous works,^{52–54} the conversion efficiency of deep-ultraviolet THG radiated from the silicon disks is much higher than that from the plasmonic gold nanostructures. Interestingly, we observe that during illumination of a train of ultrashort pulses, the THG signal progressively grows over time. The underlying mechanism is attributed to the gradual excitation of dangling bonds inside the disks by the ultrashort laser pulses with high peak intensity. The formed dangling bonds improve the third-order nonlinear susceptibility of the silicon atoms.

Methods

Sample Fabrication

A great deal of 4×4 arrays of Si disks with a period of $2\times 2\ \mu\text{m}$ were fabricated on fused silica wafers. First, 80 nm of amorphous silicon was deposited using a low-pressure chemical vapor deposition (LPCVD) technique. Then, using a standard electron-beam lithography technique, the disks were defined in a positive resist AR-P 6200 from Allresist (r), followed by electron-beam deposition of 50 nm Al and lift-off. This way, the disks are now defined in Al, thus we could etch them in Si using the BOSCH process in an ICP machine. The last step consists in removing the Al layer using a phosphoric acid water mixture. More details about the fabrication procedure can be found in Ref. 39. The SEM imaging are performed

by a focused ion beam-scanning electron microscope (FIB-SEM, Zeiss Auriga).

Numerical Simulation

We compute the field enhancement in the individual, isolated resonators with varying radius by numerically solving the time-harmonic, linear Maxwell's equations. Plane waves of various wavelengths are used as excitation, with normal incidence from the substrate. We use tabulated material data⁵⁵ for the Si disks, the substrate is modeled with SiO₂ with a constant refractive index of $n=1.5$, and the surrounding material is air, $n=1$. The field intensity in the center of the disk (at an elevation of 40nm above the SiO₂-Si interface) and the maximum normal component of the field on the disk upper surface, excluding the outer edges, are extracted from the near field solution.

For solving Maxwell's equations we use a higher-order finite-element method, implemented in the solver JCMsuite.⁵⁶ The rotational symmetry of the geometrical setup is taken into account by an self-adaptive expansion in a Fourier series in the rotation angle. Transparent boundary conditions are realized by using perfectly matched layers. High numerical accuracy is ensured by using a conservative setting of the numerical parameters (polynomial degree of the FEM ansatz functions of $p=5$ and mesh elements size smaller than $\lambda/5n$).

Third Harmonic Measurement We employ a confocal monochromatic setup (modified McPherson 234/302, 1200 lines/mm concave grating for 110–310 nm) to collect the generated THG in transmission geometry, where the generation volume acts as an entrance slit. A photomultiplier tube (Hamamatsu H8259-09) that is highly sensitive to the deep-ultraviolet wavelength range and a photon counter (Scientific Research SR400) capable of single-photon counting is used to measure the transmitted third harmonic signal. A gold parabolic mirror is employed to focus the laser pulses, which enter the sample from the side of glass substrate. The spectrum of our Ti:sapphire laser oscillator spans from 650 to 1000 nm. The repetition rate of the oscillator is 100 MHz. Broadband double-chirped mirrors and a pair of fused silica wedges are employed to control the dispersion and to measure the fundamental pulse characteristics based on the dispersion scan technique. The focal spot diameter of 7 μm is

evaluated by third harmonic z-scan method. In order to cover the entire array of silicon disks, the laser spot diameter irradiated on the silicon disks is set to $12\text{ }\mu\text{m}$ by moving the parabolic mirror.

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Figure 1: Schematic of a silicon nanodisk of diameter D and thickness t . Laser is focused onto a disk from the glass substrate side. We detect the third harmonic generation in the transmission geometry. (b,c) Calculated near-field intensity distribution of a silicon disk ($D=600$ nm, $t=80$ nm) upon normal x -polarized plane-wave at 820 nm illumination from the substrate, showing a second-order anapole state. (d) Calculated maximal amplitude $|E_z|$ at the disk's surface (blue curve) and intensity enhancement factor $|E/E_0|^2$ (red curve) at the center of the disk given in panels (b,c). Inset: Spectral intensity of our few-cycle Ti:sapphire oscillator.

Figure 2: (a) Calculated spectral distribution of intensity enhancement factor at the center of Si disks as a function of the disk diameter. Open circles correspond to the disks in panel (b), which displays a scanning electron microscopy image of a pristine array of silicon nanodisks. The numbers in (b) indicate the diameters in nanometers; the thickness of the disks is 80 nm. (c) Spectra of THG emission from the substrate (gray curve) and from the disks (red curve). Please note that we amplify the spectral intensity of THG emission from the substrate by a factor of 5 for a better visualization. The filled triangles indicate two spectral peaks. (d) Enhancement factor of THG emission from Si disks with respect to that from substrate.

Figure 3: (a) Real-time acquisition of third harmonic at 260 nm (chosen by monochromator) emission from silicon disks when pumping by 7.6 fs (red curve) and 9.5 fs (green curve) pulse train, respectively. The black curves are exponential fits. The dashed arrows indicate the time at which a new array of silicon disks is translated to the laser focus plane. The solid arrow indicates when a BK7 glass acting as a longpass filter is inserted in front of the UV detector. (b) Growth rate of third harmonic signal at 260 nm as a function of the pumping intensity. (c) The fundamental beam is blocked when the THG signal reaches zero, that is, from 3rd to 11th min. (d) A long-term of Si disks up to 160 min of continuous exposure. (e) Evolution of THG emission from a bare Si film with a thickness of 80 nm. Data in panels (c),(d) and (e) are acquired when the laser pulse duration is 7.6 fs and the corresponding peak intensity is $\sim 0.1 \text{ TW/cm}^2$.

Figure 4: Spectral intensity of third harmonic emission from a pristine array of silicon disks (dashed black curve) and from an array after long-term laser exposure (solid black curve). The THG enhancement factor (dashed dotted blue curve) is defined as the ratio between the laser-illuminated sample and the pristine one. The filled triangles indicate two local peaks of the enhancement factor. The thick gray line highlights the wavelength at 260 nm selected by a monochromator for THG intensity measurements. (b) Dependence of THG on laser polarization for pristine disks (red circles) and laser-illuminated disks (black squares). Please note that they are normalized independently. (c) Scanning electron microscopy image of an array of silicon nanodisks after 15 min of laser illumination. Optical microscopy images of the silicon disks before (d) and after (e) 15 min of laser illumination with a peak intensity of $\sim 0.1 \text{ TW}/\text{cm}^2$.

Graphical TOC Entry