Research article

Xinxiang Niu, Xiaoyong Hu*, Quan Sun*, Cuicui Lu*, Yuanmu Yang, Hong Yang and Qihuang Gong

Polarization-selected nonlinearity transition in gold dolmens coupled to an epsilon-near-zero material

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Abstract: Nonlinear optical materials are cornerstones of modern optics including ultrafast lasers, optical computing, and harmonic generation. The nonlinear

coefficients of optical materials suffer from limitations in strength and bandwidth. Also, the nonlinear performance is typically monotonous without polarization selectivity, and to date, no natural material has been found to possess nonlinear coefficients with positive or negative signs simultaneously at a specific wavelength, all of which impede practical applications in the specific scenario. Here, we realize broadband large optical nonlinearity accompanied with ultrafast dynamics in a coupled system composed of gold dolmens and an epsilon-near-zero material for dual orthogonal polarizations simultaneously. The system also shows the polarization-selected nonlinearity transition properties, where the sign of the optical nonlinear refractive indexes can be converted via polarization switching. This guarantees active transitions from self-focusing to self-defocusing by polarization rotation without tuning wavelength in practical utilizations. The measured nonlinear refractive index and susceptibility demonstrate more than three orders of magnitude enhancement over a 400-nm-bandwidth compared with the constituents, while maintaining the sub-1 ps time response. The realized enhanced, ultrafast response, and the polarization tunability ensure the designed system a promising platform for the development of integrated ultrafast laser sources, all-optical circuits and quantum chips.

Keywords: epsilon-near-zero materials; nonlinear metasurfaces; plasmonic nanoantennas; third-order all-optical nonlinearity; ultrafast photonics.

***Corresponding authors: Xiaoyong Hu**, State Key Laboratory for Mesoscopic Physics, Department of Physics, Collaborative Innovation Center of Quantum Matter & Frontiers Science Center for Nano-optoelectronics, Beijing Academy of Quantum Information Sciences, Peking University, Beijing 100871, China; Peking University Yangtze Delta Institute of Optoelectronics, Nantong, Jiangsu 226010, China; Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi, 030006, China, E-mail: xiaoyonghu@pku.edu.cn. <https://orcid.org/0000-0002-1545-1491>; **Quan Sun**, Research Institute for Electronic Science, Hokkaido University, Sapporo 001-0021, Japan; and Peking University Yangtze Delta Institute of Optoelectronics, Nantong, Jiangsu, 226010, China, E-mail: quansun@es.hokudai.ac.jp; and **Cuicui Lu**, Key Laboratory of Advanced Optoelectronic Quantum Architecture and Measurements of Ministry of Education, Beijing Key Laboratory of Nanophotonics and Ultrafine Optoelectronic Systems, School of Physics, Beijing Institute of Technology, Beijing 100081, China, E-mail: cuicuilu@bit.edu.cn. <https://orcid.org/0000-0001-7789-1946>

Xinxiang Niu, State Key Laboratory for Mesoscopic Physics, Department of Physics, Collaborative Innovation Center of Quantum Matter, Beijing Academy of Quantum Information Sciences, Nano-optoelectronics Frontier Center of Ministry of Education, Peking University, Beijing 100871, China, E-mail: xinxiangniu@pku.edu.cn

Yuanmu Yang, State Key Laboratory of Precision Measurement Technology and Instruments, Department of Precision Instrument, Tsinghua University, Beijing 100871, China, E-mail: ymyang@tsinghua.edu.cn

Hong Yang and Qihuang Gong, State Key Laboratory for Mesoscopic Physics, Department of Physics, Collaborative Innovation Center of Quantum Matter, Beijing Academy of Quantum Information Sciences, Nano-optoelectronics Frontier Center of Ministry of Education, Peking University, Beijing 100871, China; Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, China; and Peking University Yangtze Delta Institute of Optoelectronics, Nantong, Jiangsu 226010, China, E-mail: hongyang@pku.edu.cn (H. Yang), qhgong@pku.edu.cn (Q. Gong)

1 Introduction

Material's all-optical nonlinearity, i.e., the dynamic change of refractive index with an injected pump laser and the ability for wavelength conversion, is the basis for the realization of integrated all-optical switches, ultrafast laser sources, active polarization controllers, and quantum optical circuits, which are essential for building next-generation

optical signal processing systems [1, 2]. Specifically, the metrics of the nonlinear materials, including the strength and the sign of the nonlinear coefficients, dynamic response time, and nonlinearity bandwidth, determine the comprehensive performance of the realized optical system [3, 4]. Conventional nonlinear materials generally have an intrinsic contradiction associated with the realization of large and ultrafast nonlinearity simultaneously. This is because the use of electron interband transitions for nonlinearity enhancement can markedly slow down the dynamic relaxation [5, 6]. Furthermore, this impedes the practical application of the all-optical nonlinearity. In addition, the sign of the nonlinear coefficients in conventional optical materials is determined by the physical origin of the nonlinearity, to be either positive or negative. Epsilon-near-zero (ENZ) materials, which show a vanishing real part of permittivity [7–10], provide some of the strongest as well as fastest optical nonlinearities compared with wide-bandgap semiconductors, atomically thin two-dimensional materials, noble metals, and organic materials [11–14]. Inside ENZ materials, the nonlinear coefficients are enhanced because of the vanished linear permittivity and the field localization [15, 16]. Interestingly, such field localization and enhancement originate from the continuity requirement of the displacement field, and the ENZ materials simultaneously have a large nonlinear coefficient and ultrafast response time [15]. However, this intense and ultrafast nonlinearity can only be observed with *p*-polarized (transverse magnetic, TM) incident light. In addition, the signs of the nonlinear coefficients for the orthogonal polarizations are identical and cannot be tuned.

Plasmonic nanoantennas can tightly confine the incident energy into the subwavelength region and allow engineered light–matter interactions mediated by plasmonic resonances, which are quite sensitive to the material itself and the surrounding environment [17]. Apart from natural materials, the nonlinear optical response has also been proposed for these metamaterials and demonstrated by controlling the change in transmission and reflection [18–20]. In most of these cases, the change physically originates from interband absorption of the plasmonic metals, which restricts the applied wavelength range. Furthermore, the nonlinear coefficients are relatively small in noble metals. Recently, a nonlinear system composed of dipole nanoantennas placed on an ENZ film was proposed by Alam et al. [21]. In that system, the arrayed nanoantennas functioned as a sensitive refractive index sensor to detect a change in the refractive index of the ENZ material. Benefitting from the large nonlinearity of the introduced ENZ material and the strong near-field

localization provided by the nanoantenna resonances, the nonlinearity of the system is larger than that for other metamaterials utilizing metals' nonlinearity. The dynamic response time can also maintain at a sub-1 ps timescale. However, the large ultrafast nonlinearity only occurs when the polarization is parallel to the long axis of the nanoantenna. Similar to unstructured ENZ films, the effective nonlinear coefficient of the coupled system is highly anisotropic. This hinders practical applications such as polarization multiplexing, which is often desired in high-capacity optical networks.

In this work, we propose a material system formed by composite gold dolmen nanostructures that are strongly coupled to an ultrathin ENZ film placed beneath, and it demonstrates simultaneous large and ultrafast all-optical nonlinearity in both the orthogonal polarizations in a broadband spectral range simultaneously. This nonlinear performance is originated from the strong coupling between the adopted gold dolmens and ENZ film [22]. Apart from the value enlargement, the sign of the nonlinear refractive indexes for two orthogonal polarizations can be designed to be opposite at a given wavelength. Specifically, in the wavelength range from 1250 to 1300 nm, the self-focusing can be actively switched to self-defocusing by rotating incident polarization in our system. The measured intensity-dependent refractive index n_2 is determined to be in the scale of $10^{-9} \text{ cm}^2/\text{W}$ for both orthogonal polarizations; this was an increase of more than three orders of magnitude compared with the bare ENZ film at the same incident conditions. Benefitting from efficient coupling between the plasmonic and ENZ modes, the large nonlinearity and sign-controlled is realized in a broadband range, which covers the entire measured 400-nm-range. This provides the possibility for application in all-optical processing chips supporting wavelength-division multiplexing and partial division multiplexing with high capacity. The large, broadband, and sign-controlled nonlinearity is accompanied by sub-1 ps ultrafast modulation (recovery time ~ 560 and ~ 370 fs for the two polarizations, respectively), indicating a processing speed exceeding 1 THz without polarization limitation. The effective third-order nonlinear susceptibility also provides a greater than 25000-fold enhancement with polarization insensitivity, as demonstrated through the third-harmonic generation measurements. Our system opens up opportunities for on-demand engineering a large ultrafast broadband optical nonlinear response accompanied with a positive or negative sign of nonlinear coefficients by polarization switching. This lays the foundation for applications including ultrafast polarization control, all-optical active networks, and integrated quantum optics.

2 Results and discussion

2.1 Sample configuration

The nonlinear material platform designed and investigated in this study is an array of gold dolmen nanostructures placed on an ultrathin ENZ film, as schematically shown in Figure 1A. Each gold dolmen is composed of a planar nanorod monomer and a nanorod dimer placed perpendicularly with the same height of 30 nm, as indicated in Figure 1B. The monomer nanorod and each nanorod in the dimer have in-plane dimensions of 320×108 and 110×283 nm², respectively. The ENZ layer placed beneath is a 20-nm-thick indium tin oxide (ITO) film deposited by magnetron sputtering on a silica substrate, with the measured dispersion curves via ellipsometry (SE 850 DUV, SENTECH GmbH, Germany) plotted in Figure 1C. The real part of the permittivity vanishes at a wavelength of 1360 nm, corresponding to the ENZ wavelength. At the ENZ wavelength, the imaginary part of the permittivity is around 0.38. The array of the dolmen nanostructures was subsequently patterned on top of the ITO film based on electron beam lithography (E-Line Plus, RAITH, Germany) followed by metal evaporation and lift-off process. The top-

view scanning electron microscopy (SEM) image of the fabricated sample is shown in Figure 1D. As evident in this figure, the gold nanostructures and the ENZ layer are uniform and in good quality. The dolmen nanostructures are periodically repeated in a two-dimensional square array in a 500×500 μm^2 area, with a pitch size of 500×600 nm². This pitch size can balance the influence of near-field interactions between the adjacent unit cells and field enhancement inside the ENZ layer. The magnified SEM image of the nanostructures is also shown. In each element, the gap size between the monomer and dimer is measured to be 32 nm, which can guarantee strong interaction between the monomer and the dimer for formation of the gap plasmon [23]. To analyze the resonant mode of the gold dolmen nanostructures, a reference sample without the ENZ layer was also fabricated by depositing the nanostructure arrays with the same dimensions directly on the silica substrate.

2.2 Linear characterization

The linear transmission spectra of the sample were measured using a homemade infrared confocal microscope

Figure 1: Sample configurations.

(A) The structure is composed of an array of gold dolmens with a height of 30 nm deposited on a 20-nm-thick indium tin oxide (ITO) epsilon-near-zero (ENZ) layer. (B) Planar structural dimensions of the gold dolmen. The pitch size is 500 nm and 600 nm along the x and y directions, respectively. (C) Measured dispersion relations of the ITO layer placed beneath. The real part of permittivity vanishes at ~ 1360 nm. The imaginary part of permittivity is 0.38 at this wavelength. (D) Top view of the scanning electron microscopy image of the fabricated sample.

with a halogen lamp as the light source. The polarization of the incident light was controlled to be parallel to the x axis and y axis marked in Figure 1B, respectively. The measured results were normalized to the silica substrate for both the x - and y polarization and are provided in Figure 2A and B, respectively. The simulated results calculated by using the finite element method (based on the commercial software COMSOL Multiphysics) are also shown. The slight deviation between the experiments and simulations might originate from fabrication imperfections. For comparison, we also measured the transmission spectra of the reference sample without the ENZ layer, and the results are shown in Figure 2C and D using x - and y polarized incident light, respectively. In the case of x -polarized incidence, two dips appear in the transmission spectrum of the reference containing gold dolmens solely. Based on the investigation of dolmen-type plasmonic nanostructures via directly near-field mapping by Yu et al. [24], these two transmission dips correspond to the bonding and antibonding modes, respectively, which are formed through the near-field strong coupling between the monomer and dimer parts, and both these modes support strong near-field localization. As for the transmission of the sample composed of the gold dolmens and the ENZ layer, the two distinct transmission dips still exist and they are blue-shifted to be centered at approximately 1130 and 1250 nm, respectively. Apart from these two dips, another dip appears at 1600 nm in Figure 2A. The inserted layer also supports the eigenmode appearing at the ENZ wavelength, which exhibits a large density of states and homogeneously confines electromagnetic radiation within the film [25–27]. Similar to the reported strong coupling phenomena between the plasmonic dipole resonant mode and ENZ mode, the additional dip indicates the occurrence of strong coupling and corresponds with the other polariton mode [28, 29]. The anti-shift between the plasmonic mode pair and the ENZ mode indicates strong coupling-induced Rabi splitting, and the wavelength separation of the two branches is larger than the 3 dB linewidth of the antenna resonances alone. For y -polarized incident light without the ENZ layer, the transmission spectrum indicated in Figure 2D exhibits a single dip at 1125 nm, corresponding to the coupled dipole resonance of the two parallelly placed nanorods in the dimer part. As comparison with Figure 2B, with insertion of the ENZ layer, strong coupling-induced splitting shifts the dip to 1050 nm and the other dip appears at 1590 nm, with a separation that is also larger than the 3 dB linewidth of the original resonances. (See Figures S1–S5 in Supplementary Material). To further confirm the existence of strong coupling in both polarization states in our system, we calculated the transmission spectra by sweeping the

spectral position of the ENZ mode, and the results are shown in Figure 2E and F for the x - and y - polarizations, respectively. In both the polarization states, the resonance modes of the plasmonic nanostructures can be curved and anticrossed with the ENZ mode, illustrating the effective energy coupling and oscillation of the system for both polarizations. We also note that for the x -polarized incidence, both the plasmonic modes involved can simultaneously strongly couple with the ENZ mode. This illustrates that strong coupling occurs among all three modes involved. The introduction of strong coupling can broaden the spectral range with near-field localization, which is vital for the realization of large broadband nonlinearity with both polarizations.

The nonlinear origin of our coupled system is schematically illustrated in Figure 2G. In the spectral region with resonances, the effective refractive index changes dramatically versus wavelength. Owing to the plasmonic-ENZ strong coupling, the resonances of the system became relatively sensitive to the refractive index of the ENZ medium. Therefore, with an injected pump laser, small changes in the refractive index of the ENZ film resulted in a spectral shift of the system's resonances for both the polarization states. Similarly, the dispersion curves in this situation are also spectrally shifted. As a result, compared with the bare ENZ material, the changes in the refractive index and the retrieved nonlinear coefficients of the coupled system are greatly amplified because of resonance modifications. Owing to the occurrence of the plasmonic-ENZ strong coupling for both x - and y polarizations in the designed system, large nonlinearity can be acquired in the two orthogonal polarization states simultaneously. Additionally, the dolmens have different responses for the two orthogonal polarizations, and resonant responses determine the sign of the nonlinear coefficients. Therefore, the relative sign of the nonlinear coefficients for the two orthogonal polarizations can be controlled to be the same or opposite on demand; this can be accomplished by just changing the wavelength or varying the geometrical dimensions of the dolmens.

2.3 Field localization and enhancement

Another vital aspect for promoting the optical nonlinear performance of our system is to effectively couple the incident energy into the ENZ layer below via strong coupling. Benefitting from the strong coupling for both incident polarization states, our system removes the obstacle of impedance mismatch and realizes normal incidence energy coupling inside the ENZ layer and overall

Figure 2: Linear optical properties.

The measured and simulated transmission spectrum of the sample with x-polarized (A) and y-polarized (B) incidence. The measured and simulated transmission spectrum of the reference without the insertion of the epsilon-near-zero (ENZ) layer with x-polarized (C) and y-polarized (D) incidence. (E) Numerical calculations of linear transmission with varied ENZ wavelengths of the indium tin oxide (ITO) layer with x-polarized incidence. (F) Numerical calculations of linear transmission with varied ENZ wavelengths of the ITO layer with y-polarized incidence. The black dashed lines in (E) and (F) represent the spectral location of the ENZ mode in the bare ITO film. (G) Schematic of the origin of nonlinear refractive index enhancement and tunability of the relative sign between the two polarization states.

nonlinearity enhancement at an arbitrary polarization state. In Figure 3A and B, we report the calculated normalized energy density in our strongly coupled system at a wavelength of 1250 nm for x polarization and 1050 nm for y polarization. The plotted $|E|^2$ -field distribution is normalized to the input $|E_0|^2$ distribution of the pure air environment. At the plotted wavelengths, for x polarization, the field is mainly distributed to form a gap plasmon between the monomer and the dimer antenna. In contrast, for y polarization, the dipole mode is observed and the field is distributed at the two ends of the dimer nanorods. Under both the orthogonal polarized excitations, the field is localized inside the ENZ layer with a several-hundred-fold near-field enhancement. To further illustrate the role of the dolmens in field enhancement, Figure 3C and D shows the energy density normalized to the situation with only the bare ENZ film along the vertical lines presented in Figure 3A and B (white dashed lines), respectively. With the aid of the nanostructures, the field intensity is enhanced by a factor greater than 600 (for x polarization) and 400 (for y polarization). Although there exists exponential decays of electromagnetic field inside the ENZ layer, the nature of ultrathin thickness of the ITO film guarantees that field enhancement can still be maintained at the same order of magnitude at the bottom of the ENZ layer for both polarizations. To characterize the wavelength dependence of such field localizations and enhancements, the energy density of the ENZ layer in the system for both polarizations is plotted in Figure 3E. The curves indicate that for either polarization, the field intensity enhancement was 100-fold greater with respect to the bare ITO over a bandwidth >600 nm. The large, broadband field enhancement for an arbitrarily polarized incident light is helpful for promotion of the nonlinear responses, which can enlarge the value of n_2 for both the x - and y polarizations by orders of magnitude.

2.4 Optical nonlinear coefficients and time response

To experimentally characterize the third-order nonlinearity of the fabricated sample, a series of Z-scan measurements was performed for simultaneously detecting the open-/closed-aperture signal at different wavelengths [30]. The light source was an optical parametric amplifier (OPA, TOPAS, Light Conversion, USA) pumped by a Ti:sapphire amplifier system (Legend Elite, Coherent, USA) operating at a 1 kHz repetition rate. The beam quality and collimation were optimized by a spatial filter, and the polarization state

was controlled by a Soleil–Babinet compensator followed by a polarizer. An achromatic doublet lens with antireflection IR coating was used to focus the incident beam at the micrometer scale, and the incident peak power intensity was characterized by power meter and knife edge measurements. The measurement was conducted with normal incidence from 1150 to 1550 nm in 25 nm increments. The Z-scan measurements can directly determine both the sign and value of the nonlinear refraction index, n_2 , and the nonlinear absorption coefficients, β , which are related to the real (n) and imaginary (α) part of the intensity-dependent complex refractive index, as analytically expressed by: $n(I) = n_0 + n_2 I$ and $\alpha(I) = \alpha_0 + \beta I$, where n_0 and α_0 represent the linear index and I is the intensity of incident light. The measured n_2 and β for incidence with the x -polarized light in this range are shown in Figure 4A and B, respectively. Considering the damage threshold of the involved materials, we maintained the incident intensity at the focus nearly constant at $I \approx 30 \text{ MW/cm}^2$ for all wavelengths. For the y -polarized incidence, the measurements were conducted with the same intensity and the results are shown in Figure 4C and D for n_2 and β , respectively. We also plotted the calculated results based on the metamaterial homogenization method [31]. In the theoretical predictions, the ITO's permittivity was described by the Drude model through the expression $\varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$, where ε_∞ is the high-frequency limit of the permittivity, ω is the angular frequency of light, ω_p is the plasma frequency which is determined by the free carrier concentrations of the material and γ is the damping rate. For accurate predictions, both the ω_p and the γ was considered to be changed in the nonlinear state of the hybrid system with pump injection [32]. The experimental results can well reproduce the variation trends predicted theoretically. For comparison, similar Z-scan measurements were performed for a pure ITO film with the same thickness (Figure S6). Over the entire measured range from 1150 to 1550 nm, the n_2 of our sample is greatly enhanced compared with the pure film for both x - and y -incident polarizations. The maximum measured value of n_2 appears at 1275 nm for the x -polarized state and is determined to be $-9.69 \times 10^{-9} \text{ cm}^2/\text{W}$. This value is four orders of magnitude larger than that measured for the bare ITO film. Over the whole measured region, the n_2 for both the x - and y -polarized states shows a relatively large value in the order of $10^{-9} \text{ cm}^2/\text{W}$. Such large values over a broad range originate from strong coupling-induced broadband field enhancement for both polarizations simultaneously. Apart from measuring the value of the nonlinear coefficients, their sign was also characterized and the results indicate

Figure 3: Field enhancements.

(A) Simulated normalized energy density (calculated as the $|E|^2$ -field distribution normalized to the input $|E_0|^2$) of the sample with x-polarized incidence at 1250 nm. (B) Simulated normalized energy density (calculated as the $|E|^2$ -field distribution normalized to the input $|E_0|^2$) of the sample with y-polarized incidence at 1050 nm. Factor of field intensity enhancement of the sample compared with the bare indium tin oxide (ITO) with x-polarized (C) and y-polarized (D) incidence. The lines of (C) and (D) are plotted along the position of the sample indicated as the dash blue lines in (A) and (B), respectively. (E) The normalized energy density inside the epsilon-near-zero (ENZ) layer versus wavelength calculated with both polarized incidences.

Figure 4: Nonlinear measurements.

Measured effective nonlinear refractive index n_2 by the closed-aperture Z-scan technique with x-polarized (A) and y-polarized (B) incidence. Measured effective nonlinear absorption β by the open-aperture Z-scan technique with x-polarized (C) and y-polarized (D) incidence. (E) Temporal change of transmittance by degenerate pump–probe measurement with x-polarized incidence. The recovery time is fitted to 560 fs. (F) Temporal change of transmittance by degenerate pump–probe measurement with y-polarized incidence. The recovery time is fitted to 370 fs.

that the relative sign with the two orthogonal polarizations can be controlled. For $\lambda = 1150$ and $1250 \text{ nm} \leq \lambda \leq 1300 \text{ nm}$, the sign of n_2 for the two polarizations are opposed, while for $1175 \text{ nm} \leq \lambda \leq 1225 \text{ nm}$ and $\lambda \geq 1325 \text{ nm}$, the two coefficients have the same sign and the same order of magnitude. For the nonlinear absorption β , the values also show broadband enhancement for both polarization states simultaneously, which is orders of magnitude larger than the bare film. The maximum value was measured as $7.23 \times 10^5 \text{ cm/GW}$ at 1300 nm for x -polarized incidence. In addition, similar to the properties of n_2 , the sign relation for the orthogonal polarizations also varies as a function of the incident wavelength. Therefore, in addition to the wavelength, the nonlinear response of our system can be modulated by switching the polarization state. Such nonlinear properties differ from the gold and ITO host materials, where the nonlinear coefficients have the same sign with different polarizations.

The temporal dynamics of the entire system are primarily dominated by both of the relaxation dynamics of the host ITO material, as well as the photon lifetime of the strongly coupled resonance modes. With an infrared pump laser, ITO can show fs-scale ultrafast dynamics via intra-band transitions of free carriers [33]. The introduced resonances, however, can increase the photon lifetime and increase the entire system's response time. To determine the response time of the entire system, degenerate pump-probe transmittance measurements at a wavelength of 1180 nm with x -/ y -polarizations were performed, respectively, and the results are displayed in Figure 4E and F. For both polarization states, the measured wavelength is located in the range with coupled plasmonic resonances, and therefore the response here can reveal the time dynamic of the system. In these measurements, the pump and probe beams are set with the same polarization state, and they are slightly angularly separated for isolating the probe beam solely. On injection of the pump, both polarizations show a temporary fall with subsequent recovery. The fall time in the two scenes is almost the same at $\sim 180 \text{ fs}$. The recovery time is exponentially fitted to be 560 fs (x polarization) and 370 fs (y polarization), respectively. Indeed, the time response is slowed down by the resonance compared with the bare film (Figure S7); however, the total response times (rise time plus the recovery time) for the two polarizations still maintain their sub-1ps ultrafast properties. This can be attributed to the relatively fast dephasing time of the involved plasmonic modes, and therefore the nonlinear system can be designed for all-optical signal processors with a speed exceeding 1 THz , which is much faster than existing processors where the signal is carried by electrons [34].

2.5 Third-harmonic generation

The effective third-order susceptibility $\chi^{(3)}$ of the hybrid system also displays broadband enhancement without polarization limitation, as characterized by third-order harmonic generation (THG). The generated THG signal from the sample was measured using a homemade confocal microscope with an objective ($50\times$, $\text{NA} = 0.48$), and the transmitted signal was coupled to a fiber optic spectrometer (AVASPEC-3648, Avantes, USA) and a visible electron-multiplying charge-coupled device (EMCCD, iXon888, ANDOR, United Kingdom) switched by a moveable mirror for spectral and intensity characterizations, respectively. The transmitted nonlinear spectrum with an excitation wavelength of 1200 nm on x polarization is shown in Figure 5A. For comparison, the transmitted signal through the reference without the ENZ layer was also measured. For the sample, a signal peak at 403 nm is observed; in contrast, no distinct signal can be observed for the reference without the ENZ layer. This indicates that the measured THG signal of the sample is generated from the ITO layer, and the role of gold dolmens is to enhance the field intensity via boosting field coupling. This is in agreement with reports showing that the nonlinear susceptibility of ITO is many orders larger than that of gold in the measured range [35]. The dependence of the generated signal on the excitation power of the sample is shown in Figure 5B, and it displays a cubic relationship. The incident wavelength was set to be 1200 nm at x polarization. This illustrates that the observed signal is indeed generated through the THG process, which is dominated by $\chi^{(3)}$ of the nonlinear platform. To quantitatively analyze the THG enhancement in our system, we swept the excitation wavelength from 1150 to 1550 nm and recorded the intensity ratios of the THG signal generated between our system and the bare ENZ film for dual polarizations. The excitation intensity at each wavelength is maintained constant at $\sim 160 \text{ MW/cm}^2$, and the results are shown in Figure 5C. The THG signal has a maximum enhancement factor exceeding 24000 at 1275 nm with x -polarized incidence, and this factor also exceeds 12000 for the y polarizations at 1150 nm . In the entire measured spectral range, the THG signal for both polarizations is enhanced by over three orders of magnitude. The experimental measured average power of the third harmonic reaches to maximum with a characterized conversion efficiency around 3.7×10^{-8} at 1275 nm . In the bare ITO film, the nonlinear frequency conversion is generally occurred at oblique incidence, by utilizing the material's anisotropy of the nonlinear response and the enhancement of the incident field due to the continuity of the electric field components

normal to the interface [7–9]. While at normal incidence, the nonlinear conversion is extremely weak because the incident electric field components parallel to the interface is insufficient localized into the ITO and weakly participated into the conversion processes [36, 37]. By involving the plasmonic nanoantennas and utilizing the energy transferring through strong coupling process, our hybrid platform overcomes this incident angle constraint and realizes a comparable THG conversion efficiency at normal incidence to the bare ITO film with higher pump intensity and oblique incidence [38]. Considering the conversion efficiency of the THG is in relation to the power of the fundamental wave, the conversion efficiency of our hybrid system could be further improved by increasing pump intensity. Since the intensity of the THG signal is in proportion to the $\chi^{(3)}$, such a large enhancement indicates that the effective $\chi^{(3)}$ of the coupled hybrid system is also enlarged by three to four orders of magnitude compared with the bare film over a broadband range for both polarization states (Figure S8 and S9). The dual-polarization THG

enhancement can also help enhance the polarization-insensitive light generation process. Figure 5D shows the intensity of the polarization-dependent THG of the sample by rotating the polarizations at 1200 nm. The intensity of the THG signal is very close for any incident polarization, owing to the similar field enhancement factors shown in Figure 3E. The large broadband enhancement and polarization-insensitive THG process indicates that our system can be applied in light sources with ultrasmall footprints, which is also an urgent need for the realization of all-optical chips.

2.6 Discussions

Compared with bare ENZ systems, the measured nonlinear responses indicate that the introduction of dolmen nanostructures in our design can simultaneously eliminate the constraints of bandwidth and polarization dependence and further enlarge the nonlinear coefficients, while still

Figure 5: Third-order harmonic generation (THG) measurements.

(A) Transmitted spectrum of the generated THG signal with the fundamental wavelength of 1200 nm at TM polarization. (B) Power-dependent relation of the generated THG in (a), the fitted slope is 2.79. (C) THG enhancement factor of the sample compared with the bare indium tin oxide (ITO) film. The measured wavelength ranges from 1150 to 1550 nm. (D) Intensity of the THG with varied polarization angle when pumping at 1200 nm.

maintaining an ultrafast dynamic time response. With respect to the nonlinear refractive index, the largest nonlinear refractive index n_2 of the ITO film with an ENZ response was reported to be $1.1 \times 10^{-10} \text{ cm}^2/\text{GW}$ [15]. However, on the one hand, this coefficient was acquired only for transverse magnetic polarized illumination and the incident angle had a tilt at 60° . For another orthogonal polarization, the ENZ response and the continuity of the displacement field could not support field localization inside, and therefore the nonlinear coefficient was lowered by several orders. On the other hand, this enlarged coefficient was limited by the incident angle and the specific ENZ wavelength. The value of n_2 dropped quickly on moving away from the ENZ wavelength or the required oblique incident angle. In contrast, the maximum measured n_2 in our system with the introduced dolmen nanostructures is $-9.69 \times 10^{-9} \text{ cm}^2/\text{W}$, which is an almost 100-fold increase. Furthermore, compared with plasmonic nonlinear metamaterials, our system utilizes the ITO's nonlinearity via intraband transitions rather than the metal's nonlinearity itself, and the nonlinear refractive index is larger by two orders of magnitude [39]. Moreover, the adopted dolmen can provide stronger near-field localization, and therefore the reported measured n_2 is also larger than that of a configuration composed of nanorod antennas coupled to ENZ films [20]. Not only is the promotion of the nonlinear coefficients, but this large nonlinearity is also no longer constrained by the polarization selection. The nonlinearity enhancement can only be provided for one fixed polarization in all systems mentioned above, while in our system, the large nonlinearity is maintained for both polarizations over a 400-nm broadband range. The introduction of composite coupled resonators can, in principle, also be used in highly doped semiconductors and transition metal nitrides, where the ENZ response appears in other parts of the spectral range; therefore, the broadband nonlinearity enlargement without polarization limitation can be realized at the desired wavelength range via this proposed mechanism [40, 41].

Similarly, with respect to harmonic generation, the demonstrated system is also no longer constrained by the polarization and tilt incidence and provide higher conversion efficiency. The measured third harmonic generation spectra were confirmed to have been improved via ENZ-enhanced nonlinearities in the natural (unstructured) ENZ material [42]. Recently, it also has been demonstrated that the conversion efficiency of the ENZ-boosted high-harmonic generation in the ultrathin film was comparable to the macroscopic conventional nonlinear media [43]. While such high efficiency was also limited to transverse magnetic polarization with tilt incidence and suffered from a narrow

bandwidth. Although structural patterned ENZ materials have been proposed, the requirement for polarization selection still urgently needs to be addressed for harmonic generation [44, 45]. In contrast, our plasmonic-ENZ composite system can provide THG generation without polarization limitations, and it is not limited to within the ENZ range. Surprisingly, the intensity of the generated signal also undergoes an enhancement by orders of magnitude.

Looking beyond the ENZ system, the nonlinear performance of our system is also markedly enhanced, and at the same time, introduces the freedom to tune the relative sign of the optical nonlinear coefficients by rotating the polarization. Comparing the nonlinear coefficients with other conventionally used nonlinear materials with an ultrafast time response, the measured n_2 of our system is seven orders of magnitude larger than that of glass, six orders of magnitude larger than that of silicon, and four orders of magnitude larger than that of a chalcogenide in a similar spectral range [46]. More importantly, in the community of optical nonlinear materials, the sign of the nonlinear coefficients and the modulation behavior with respect to the incident light (such as self-focusing/self-defocusing, saturated absorption/reverse saturated absorption) is insensitive to the incident polarization, which is because they are determined by the materials' lattice structures. While from the perspective of practical utilizations, material systems with adjustable positive/negative refractive indexes are in highly demand. By introduction of coupled dolmen nanostructures, our system overcomes this limitation and acquires nonlinear coefficients with opposing signs for the two orthogonal polarized incidences. This indicates that self-focusing or self-defocusing and saturated absorption or reverse saturation absorption can be switched by just rotating the incident polar angle at a given wavelength. Such large polarization tunable nonlinearity with broadband and ultrafast responses can be used to realize polarization switching, polarization mode selectors, and function as the cornerstone for all-optical polarization multiplexed signal processing systems with enhanced processing capacity and for single-mode ultrafast laser sources.

3 Conclusions

In conclusion, we propose a coupled optical nonlinear system by introducing dolmen nanostructures on top of an ultrathin ITO layer with ENZ response. We show the optical nonlinearity is simultaneously magnified and broadened for both the orthogonal polarization states. The measured a maximum nonlinear refractive index is $-9.69 \times 10^{-9} \text{ cm}^2/\text{W}$, which is enhanced by four orders of magnitude compared

with the bare ITO film. Furthermore, in a 400-nm-bandwidth measurement range, this coefficient with a large enhancement can be maintained without polarization limitation. We also demonstrate that the nonlinearity transition with the sign of the optical nonlinear coefficients can be realized via polarization switching, ensuring active transitions from self-focusing to self-defocusing by polarization rotation. The enhanced nonlinearity is accompanied by an ultrafast temporal response that was on the order of a few hundred femtoseconds for both polarizations, and therefore it allows light modulations at ultrafast rates exceeding 1 THz. The effective $\chi^{(3)}$ also owns a large enchantment without polarization limitation, which results in polarization-insensitive THG generation. Therefore, the designed system is suitable for wavelength and polarization sensitive applications and removes the general reliance on the energy band structure for conventional nonlinear materials. The results of this work pave the route for applications in integrated optics, nonlinear optics, and quantum optics as nonlinear components for the realization of all-optical processors, quantum chips, and tunable integrated light sources.

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