

Enhanced Optical Nonlinearities in Epsilon-Near-Zero Nanostructures

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*To my family, for their unwavering support,
and in loving memory of my father.*

Abstract

In a vacuum, light-by-light interactions require extremely high field strengths. However, when mediated by matter, these interactions require significantly lower intensities that are readily accessible with pulsed lasers. Nonlinear optics studies how intense optical fields modify the optical properties of materials and the resulting light-matter interactions. Among these, third-order optical nonlinearities play a central role in technologically relevant applications, such as third-harmonic generation, four-wave mixing, optical switching, and supercontinuum generation, among many others.

Materials operating in the epsilon-near-zero (ENZ) region provide an attractive platform for exploring strong nonlinear light-matter interactions. Near the ENZ wavelength, the real part of the permittivity approaches zero, leading to a small linear refractive index and enhanced optical fields at the interface due to boundary conditions. Transparent conducting oxides such as indium tin oxide (ITO) have the real part of permittivity approaching zero in the near-infrared and exhibit a nonlinear refractive index coefficient (n_2) approximately five orders of magnitude larger than that of conventional dielectrics. This dissertation, titled **Enhanced Optical Nonlinearities in Epsilon-Near-Zero Nanostructures**, explores nonlinear phenomena in ITO-based thin films and nanostructures in the ENZ region. This thesis begins with an overview of ENZ materials and their optical nonlinearities, with emphasis on prior work in ITO that motivates the nonlinearities explored in the subsequent chapters.

The first part of the thesis investigates nonlinear light-matter interactions in subwavelength-thick ITO films. We demonstrate, both theoretically and experimentally, that frequency-degenerate pump and probe pulses can undergo coherent energy transfer in the ENZ region of ITO. Unlike conventional two-beam coupling, which requires an initial frequency difference or chirp between the interacting beams, here the large and ultrafast refractive-index modulation of the ENZ medium induces the frequency shifts needed for energy transfer. Remarkably, the probe gain scales quadratically rather than linearly with the product of the pump intensity and the nonlinear refractive index coefficient ($n_2 I$), transitioning from conventional two-beam coupling to a regime dominated by time-refraction.

The next part of the thesis explores how engineering the longitudinal electric field in ENZ structures provides an effective strategy for enhancing third-order nonlinear interactions. Using

ITO both as the nonlinear material and as a partial reflector, we designed ITO–SiO₂–Au Gires–Tournois nanocavities. By engineering the cavity spacer thickness to support a resonant cavity mode in the ENZ region, we excite a Brewster mode within the ITO layer. This leads to strong longitudinal electric-field enhancement with a uniform E_z field distribution inside the nonlinear material, ITO. Optical pumping enables dynamic tuning of the Brewster resonance by approximately 170 nm with an on–off contrast of about 25 dB, demonstrating the potential for ultrafast all-optical switching.

The strong angle-dependent field enhancements of the Brewster mode and the nanocavity mode enable us to achieve unity-order four-wave mixing (FWM) with a conversion efficiency of 45% when the pump and signal are frequency-degenerate. When the pump and signal are nondegenerate, the device supports a four-wave mixing bandwidth of approximately 70 nm spanning the telecommunications O-band, indicating that the intrinsic nonlinear response time of ITO is on the order of tens of femtoseconds. Our results establish ITO films as a nanophotonic platform for free-space multimode signal processing with structured light, real-time holography, and quantum optics.

The later chapters of the thesis explore nonlinear light–matter interactions in ultrathin ENZ films. Ultrathin ENZ films support both radiative Ferrell–Berreman modes and confined ENZ modes, both of which are associated with strong longitudinal electric fields. By engineering ITO–Si bilayer structures to excite the Berreman mode primarily from one excitation direction, we show that this results in asymmetric longitudinal field enhancement. This asymmetry leads to a direction-dependent nonlinear response, resulting in a nonreciprocal transmission ratio of approximately 2.0 through purely passive nonlinear effects. In addition, we show that the spectral and angular bandwidth of this nonreciprocal response follows the ENZ spectral region, where absorption and field enhancement are strongest.

Finally, we investigate nonlinear metasurfaces formed by plasmonic nanoantennas patterned atop an ultrathin ITO film. The metasurface is designed to strongly couple the localized surface plasmon resonance of the Au nanoantennas to the ENZ mode of ITO. By adjusting the relative phase between the two counter-propagating input beams, we demonstrate coherent perfect absorption and show how this response can be dynamically tuned by optical pumping. In addition, this thesis also includes two collaborative studies presented in the appendices. The first introduces Fourier lattice resonances (FLRs) in plasmonic metasurfaces and demonstrates how the nanoparticle arrangement can be determined prior to the fabrication based on the desired resonance wavelengths. The second focuses on dielectric metasurfaces on ultrathin ITO films, examining the interaction between Mie resonances and the ENZ mode and its impact on nonlinear response.

Together, these results demonstrate that ENZ nanostructures provide a useful platform for study-

ing strong nonlinear light–matter interactions in subwavelength and ultrathin structures. The work presented in this thesis shows that the large and ultrafast nonlinear response of ITO in its ENZ region can be harnessed in engineered nanostructures to realize parametric amplification, efficient four-wave mixing, nonlinear nonreciprocal transmission, and dynamically tunable coherent perfect absorption.

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List of Publications

I contributed to the following publications during my graduate studies at the University of Ottawa, Department of Physics.

Peer-reviewed Journal Publications

1. Rasoul Alaei, **Yaswant Vaddi** & Robert W. Boyd. Dynamic coherent perfect absorption in nonlinear metasurfaces. *Optics Letters* **45**, 6414–6417 (2020).
2. Theng-Loo Lim, **Yaswant Vaddi**, M. Saad Bin Alam, Lin Cheng, Rasoul Alaei, Jeremy Upham, Mikko J. Huttunen, Ksenia Dolgaleva, Orad Reshef & Robert W. Boyd. Fourier-engineered plasmonic lattice resonances. *ACS Nano* **16**, 5696–5703 (2022).
3. Mohammad Karimi, Kashif Masud Awan, **Yaswant Vaddi**, Rasoul Alaei, Jeremy Upham, M. Zahirul Alam, & Robert W. Boyd. Interactions of fundamental Mie modes with thin epsilon-near-zero substrates. *Nano Letters* **23**, 11555–11561 (2023).
4. **Yaswant Vaddi**, Theng-Loo Lim, Yiyu Zhou, Mohammad Karimi, Shivashankar Vangala, Jeremy Upham, Joshua R. Hendrickson, Robert W. Boyd, and M. Zahirul Alam. Parametric amplification of optical pulses through synthetic motion in a time-varying medium. *Nano Letters* **26**, 8635–8641 (2026). (*Selected as Front Cover Art*)

Manuscripts in Preparation

1. **Yaswant Vaddi**[†], Theng-Loo Lim[†], Rasoul Alaei, Shivashankar Vangala, Jeremy Upham, Yaryna Mamchur, R. Margoth Córdova-Castro, Joshua R. Hendrickson, Robert W. Boyd, and M. Zahirul Alam. Unity-order efficiency wave mixing in epsilon-near-zero nanostructures ***Manuscript in preparation***

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3. **Yaswant Vaddi**, Diego M. Solís, Shivashankar Vangala, Joshua R. Hendrickson, Nader Engheta, Robert W. Boyd, and M. Zahirul Alam. Nonreciprocity in an epsilon-near-zero-dielectric bilayer structure. ***Manuscript in preparation***

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Conference Proceedings

1. Suresh, Sisira, **Yaswant Vaddi**, M. Zahirul Alam, R. Margoth Córdova-Castro, Jeremy Upham & Robert W. Boyd. Suppression of structural birefringence of plasmonic antennas by epsilon-near-zero layers. *Laser Science*, JW4A-10 (Optica Publishing Group, 2023).
2. R. M. Córdova-Castro, **Yaswant Vaddi**, C. Cabriel, D. Jonker, M. Zapata-Herrera, A. Krasavin, A. Susarrey-Arce *et al.* Single-emitter photon emission rate enhancement with nanomaterials at the super-resolution level. *Frontiers in Optics*, JTU4A-52 (Optica Publishing Group, 2023).
3. Theng-Loo Lim, **Yaswant Vaddi**, M. Zahirul Alam, Shivashankar R. Vangala, Jeremy Upham, Joshua R. Hendrickson, & Robert W. Boyd. Highly efficient degenerate four-wave mixing with an epsilon-near-zero-based low-Q cavity. *Nonlinear Photonics*, NpTh3C-5 (Optica Publishing Group, 2024).
4. **Yaswant Vaddi**, Theng-Loo Lim, M. Zahirul Alam, Shivashankar R. Vangala, Jeremy Upham, Joshua R. Hendrickson & Robert W. Boyd. An ultrafast all-optical switch with an epsilon-near-zero-based nanocavity. *Nonlinear Photonics*, NpTh3C-1 (Optica Publishing Group, 2024).
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Chapter 1

Introduction

1.1 Motivation & Scope of the thesis

Light has played a fundamental role in the evolution of the cosmos [1] and has fascinated scientists throughout history [2]. Optics studies how electromagnetic radiation behaves and, crucially, how it interacts with matter. At sufficiently low optical intensities, these interactions are well described by linear optics. The invention of the laser in the 20th century by Theodore H. Maiman [3], based on the earlier theoretical work of Charles H. Townes and Arthur L. Schawlow [4], changed this picture. Lasers enabled access to field strengths high enough to modify the optical properties of materials. Nonlinear optics studies the phenomena that result from these modifications. The field of nonlinear optics formally began in 1961, when Franken and co-workers observed second-harmonic generation [5]. Since then, it has developed into a broad field with applications in frequency conversion, ultrafast all-optical switching, optical signal processing, and parametric amplification, while also playing a central role in modern quantum optics [6, 7].

1.1. *MOTIVATION & SCOPE OF THE THESIS*

However, the nonlinear response of most optical materials is much weaker than the linear response. In particular, third-order ($\chi^{(3)}$) nonlinearities are inherently weaker than second-order processes ($\chi^{(2)}$). To compensate for this weak intrinsic response, researchers typically engineer structures — such as high-Q ring resonators, long waveguides, or slow-light structures — to accumulate a nonlinear phase shift by increasing the effective interaction length. While these approaches have been successful in integrated photonics, they often rely on complex nanofabrication and precise dispersion engineering, motivating the search for materials with stronger “intrinsic” nonlinearities.

One promising route is to use materials in their epsilon-near-zero (ENZ) region — the spectral region where the real part of the permittivity, $\text{Re}(\epsilon)$, approaches zero. This condition occurs naturally in materials where the $\text{Re}(\epsilon)$ transitions from a positive (dielectric-like) to a negative (metal-like) value. Recent experiments on transparent conducting oxides (TCOs), such as indium tin oxide (ITO) and aluminum zinc oxide (AZO), have demonstrated large third-order optical nonlinearities in this region [8, 9]. Because the ENZ wavelength of TCOs lies in the near-infrared and is compatible with existing complementary metal–oxide–semiconductor (CMOS) fabrication, it is a highly attractive platform for nanophotonic systems. Building on these observations, subsequent studies have demonstrated a variety of nonlinear phenomena in ENZ systems [10–12], including time refraction [13–15], four-wave mixing [16], third-harmonic generation [17], ultrafast all-optical switching [18], and high harmonic generation [19].

The motivation of this thesis is to pursue new regimes of nonlinear light–matter interaction in ENZ materials, specifically:

1.1. *MOTIVATION & SCOPE OF THE THESIS*

1. Parametric amplification driven by large temporal modulation of the refractive index in subwavelength-thick ENZ films (Chapter 2)
2. Ultrafast dynamics of the excitation of a Brewster mode in an epsilon-near-zero-based nanocavity (Chapter 3)
3. Unity-order wave-mixing conversion efficiencies in ENZ nanocavities driven by strong field enhancements in the ITO layer (Chapter 4)
4. Access to strong optical fields in ultrathin ENZ layers via coupling to Berreman modes in ITO–Si bilayers and to confined ENZ modes in plasmonic metasurfaces on ITO, enabling nonreciprocal response and coherent perfect absorption (Chapters 5 and 6)

The central hypothesis of this thesis is that the intrinsically strong nonlinear response of ENZ materials can be significantly enhanced by engineering their electromagnetic environment, thereby enabling regimes of spatiotemporal light control that are not accessible in conventional nonlinear materials. From planar films to more complex structures such as nanocavities, asymmetric bilayers, and plasmonic metasurfaces, these configurations enable strong field enhancement and enhanced nonlinear light–matter interactions in ENZ materials.

This first chapter introduces nonlinear optics in general, and the nonlinear optical response of transparent conducting oxides, particularly ITO, in the ENZ region. The following section begins with Maxwell’s equations and the nonlinear wave equation, and then focuses on third-order nonlinearities, especially the optical Kerr effect in conventional dielectrics.

1.2 Nonlinear light–matter interactions

Nonlinear optical phenomena arise when a material’s polarization responds nonlinearly to intense applied optical fields. To understand how nonlinear polarization generates new frequencies that serve as sources of electromagnetic fields, we first outline Maxwell’s equations, examine how nonlinear polarization enters the wave equation, and then focus on third-order light–matter interactions, which are central to this thesis.

1.2.1 Maxwell’s equations

To establish a theoretical framework for nonlinear light–matter interactions, we begin with Maxwell’s equations. In a dielectric medium, Maxwell’s equations are given by

$$\nabla \cdot \tilde{\mathbf{D}} = \tilde{\rho}, \quad (\text{Gauss’s Law}) \quad (1.1)$$

$$\nabla \cdot \tilde{\mathbf{B}} = 0, \quad (\text{Gauss’s Law for Magnetism}) \quad (1.2)$$

$$\nabla \times \tilde{\mathbf{E}} = -\frac{\partial \tilde{\mathbf{B}}}{\partial t}, \quad (\text{Faraday’s Law}) \quad (1.3)$$

$$\nabla \times \tilde{\mathbf{H}} = \tilde{\mathbf{J}} + \frac{\partial \tilde{\mathbf{D}}}{\partial t}, \quad (\text{Ampere’s Law}) \quad (1.4)$$

where for an isotropic, lossless, dispersionless, and nonmagnetic material ($\tilde{\mathbf{B}} = \mu_0 \tilde{\mathbf{H}}$) without free charges ($\tilde{\rho} = 0$) and free currents ($\tilde{\mathbf{J}} = 0$), the displacement field $\tilde{\mathbf{D}}$ and electric field $\tilde{\mathbf{E}}$ are related by

$$\tilde{\mathbf{D}} = \varepsilon_0 \tilde{\mathbf{E}} + \tilde{\mathbf{P}}. \quad (1.5)$$

1.2. NONLINEAR LIGHT-MATTER INTERACTIONS

In linear optics, the polarization is defined as $\tilde{\mathbf{P}} = \varepsilon_0 \chi^{(1)} \tilde{\mathbf{E}}$. Substituting this into Eq. 1.5, we obtain

$$\tilde{\mathbf{D}} = \varepsilon_0 \tilde{\mathbf{E}} + \varepsilon_0 \chi^{(1)} \tilde{\mathbf{E}} = \varepsilon_0 \varepsilon^{(1)} \tilde{\mathbf{E}}, \quad (1.6)$$

where $\varepsilon^{(1)}$ is the dimensionless relative permittivity of the optical material.

1.2.2 Nonlinear polarization and the wave equation

When the optical intensity becomes sufficiently high, the linear approximation for the polarization vector breaks down, as the electrons are driven far from equilibrium. In many cases, particularly in the perturbative regime, the polarization can be expressed as a power series in the electric field as

$$\tilde{\mathbf{P}} = \underbrace{\varepsilon_0 \chi^{(1)} \tilde{\mathbf{E}}}_{\tilde{\mathbf{P}}^{(1)}} + \underbrace{\varepsilon_0 \left(\chi^{(2)} \tilde{\mathbf{E}}^2 + \chi^{(3)} \tilde{\mathbf{E}}^3 + \dots \right)}_{\tilde{\mathbf{P}}^{\text{NL}}}, \quad (1.7)$$

Here, $\tilde{\mathbf{P}}^{(1)}$ depends linearly on the electric field $\tilde{\mathbf{E}}$ and corresponds to the linear response of the material. $\tilde{\mathbf{P}}^{\text{NL}}$ depends nonlinearly on the electric field $\tilde{\mathbf{E}}$ and corresponds to the nonlinear response of the material. Taking the curl of Eq. 1.3 and substituting Eq. 1.5 into Eq. 1.4, we obtain the wave equation in a medium as

$$\nabla^2 \tilde{\mathbf{E}} - \frac{1}{c^2} \frac{\partial^2 \tilde{\mathbf{E}}}{\partial t^2} = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \tilde{\mathbf{P}}}{\partial t^2}, \quad (1.8)$$

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Using $\tilde{\mathbf{P}} = \tilde{\mathbf{P}}^{(1)} + \tilde{\mathbf{P}}^{\text{NL}}$ in Eq. 1.5 and rewriting Eq. 1.8 in terms of $\tilde{\mathbf{P}}^{\text{NL}}$ leads to the generalized nonlinear wave equation as

$$\nabla^2 \tilde{\mathbf{E}} - \frac{\epsilon^{(1)}}{c^2} \frac{\partial^2 \tilde{\mathbf{E}}}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \tilde{\mathbf{P}}^{\text{NL}}}{\partial t^2}. \quad (1.9)$$

Here, the term on the right-hand side acts as a source of new electromagnetic waves, giving rise to nonlinear optical phenomena.

1.2.3 Nonlinear optical processes

As introduced in Eq. 1.7, the nonlinear polarization can be expanded in powers of the electric field. Each term in this expansion corresponds to a distinct class of nonlinear optical processes. Treating the fields as scalar quantities and assuming an instantaneous nonlinear response [6], the polarization at time t can be written as

$$\tilde{P}(t) = \epsilon_0 [\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \dots], \quad (1.10)$$

$$\equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \dots \quad (1.11)$$

Here, $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order nonlinear susceptibilities, and $\tilde{P}^{(2)}(t)$ and $\tilde{P}^{(3)}(t)$ represent the corresponding nonlinear polarizations. Second-order optical interactions occur in noncentrosymmetric materials and give rise to phenomena such as second-harmonic generation, spontaneous parametric down-conversion, and sum- and difference-frequency generation. In contrast, third-order interactions occur in both centrosymmetric and noncentrosymmetric me-

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dia and include processes such as the optical Kerr effect, four-wave mixing, and third-harmonic generation.

1.2.4 Third-order light–matter interactions and the optical Kerr effect

This thesis mainly focuses on third-order nonlinear optical processes. In this section, we describe third-order nonlinear interactions in general and, in particular, focus on the optical Kerr effect, highlighting the underlying assumptions in the standard description and noting when they break down.

The nonlinear polarization corresponding to the third-order nonlinearities is given by

$$\tilde{P}^{(3)}(t) = \varepsilon_0 \chi^{(3)} \tilde{E}^3(t). \quad (1.12)$$

When the electric field contains multiple frequency components, the nonlinear polarization contains contributions at frequencies corresponding to sums and differences of the input frequencies. Different combinations of the input frequencies correspond to distinct third-order nonlinear processes such as third-harmonic generation (THG), self-phase modulation (SPM), cross-phase modulation (XPM), and four-wave mixing (FWM). The real and imaginary parts of the susceptibility describe optically induced changes in refractive index and absorption, respectively.

All of these optical processes arise from the same third-order nonlinear susceptibility $\chi^{(3)}$, but the specific nonlinear phenomenon depends on the combination of interacting frequencies. Figure 1.1 describes the general case of frequency mixing in a nonlinear $\chi^{(3)}$ medium, where three input

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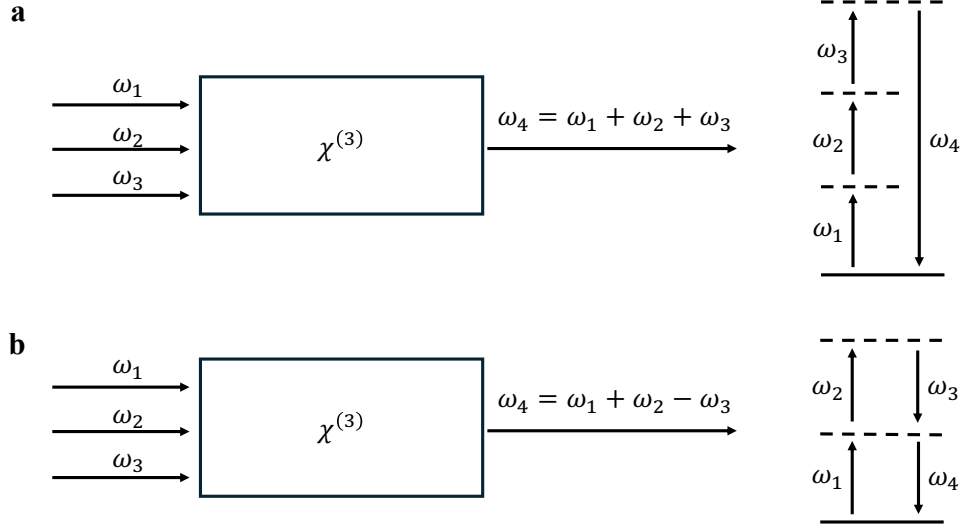


Figure 1.1: Schematic of third-order nonlinear frequency-mixing processes illustrating general four-wave mixing interactions: (a) frequency addition process $\omega_4 = \omega_1 + \omega_2 + \omega_3$, which includes special cases such as third-harmonic generation (frequency-degenerate case: $\omega_1 = \omega_2 = \omega_3 = \omega$, giving $\omega_4 = 3\omega$), and (b) frequency mixing process $\omega_4 = \omega_1 + \omega_2 - \omega_3$ (degenerate case: $\omega_1 = \omega_2 = \omega_3 = \omega$, giving $\omega_4 = \omega$).

frequencies interact to create the fourth frequency. For a monochromatic field, $\tilde{E}(t) = E_0 \cos \omega t$, the third-order nonlinear polarization simplifies to

$$\tilde{P}^{(3)}(t) = \frac{1}{4} \epsilon_0 \chi^{(3)} E_0^3 \cos 3\omega t + \frac{3}{4} \epsilon_0 \chi^{(3)} E_0^3 \cos \omega t. \quad (1.13)$$

The first term corresponds to oscillation at 3ω and leads to third-harmonic generation, as illustrated in Fig. 1.1(a) in the degenerate case. The second term oscillates at ω and corresponds to the degenerate four-wave mixing process shown in Fig. 1.1(b). Here, the nonlinear polarization

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oscillates at the same frequency as the incident field, resulting in an intensity-dependent refractive index — the optical Kerr effect.

Assuming a centrosymmetric material and treating the fields in the frequency domain, the nonlinear polarization that governs the propagation of a beam of frequency ω is therefore

$$P^{\text{NL}} = 3\varepsilon_0\chi^{(3)}(\omega = \omega + \omega - \omega)|E(\omega)|^2E(\omega), \quad (1.14)$$

where the factor of 3 arises from the number of permutations of identical frequency components in the degenerate interaction. For a monochromatic field, ignoring the tensorial nature of the susceptibility, the total polarization of the material can be written as

$$P^{\text{TOT}}(\omega) = P(\omega) + P^{\text{NL}}(\omega) = \varepsilon_0E(\omega) [\chi^{(1)} + 3\chi^{(3)}|E|^2] \equiv \varepsilon_0\chi_{\text{eff}}E(\omega). \quad (1.15)$$

The effective susceptibility is related to the refractive index as $n^2 = 1 + \chi_{\text{eff}}$, which implies

$$n = \sqrt{1 + \chi^{(1)} + 3\chi^{(3)}|E|^2} = \sqrt{\varepsilon^{(1)} + 3\chi^{(3)}|E|^2}. \quad (1.16)$$

Here, permittivity, refractive index, and susceptibility are, in general, complex quantities; in what follows, we focus on the real part governing refractive index changes. Using the plane-wave relation between intensity and field amplitude in a homogeneous medium,

$$I = 2\text{Re}(n_0)\varepsilon_0c|E|^2, \quad (1.17)$$

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Eq. 1.16 can be written as

$$n = \sqrt{n_0^2 + \frac{3\chi^{(3)}I}{2\text{Re}(n_0)\epsilon_0 c}}. \quad (1.18)$$

If the nonlinear contribution is small compared to the linear contribution, the square root can be expanded to first order,

$$n \approx n_0 + \frac{3\chi^{(3)}I}{4n_0\text{Re}(n_0)\epsilon_0 c}. \quad (1.19)$$

This perturbative approach is valid only when

$$\left| \frac{2n_2 I}{n_0} \right| \ll 1, \quad (1.20)$$

where the nonlinear refractive index is defined as

$$n_2 = \frac{3\chi^{(3)}}{4n_0\text{Re}(n_0)\epsilon_0 c}. \quad (1.21)$$

The refractive index in the presence of an intense optical field is therefore

$$n = n_0 + \Delta n = n_0 + n_2 I, \quad (1.22)$$

where n_0 is the linear refractive index, n_2 is the nonlinear refractive index coefficient, and I is the optical intensity. This derivation assumes that the same optical field both induces and probes the refractive index change.

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For sufficiently strong nonlinear responses, the perturbative approximation given in Eq. 1.20 can break down, particularly when the linear refractive index becomes small. As introduced in Section. 1.1, in ENZ materials, where the combination of large nonlinearities and a small linear refractive index leads to $|2n_2 I/n_0| \not\ll 1$. In this regime, the perturbative expansion is no longer valid, and the full expression for n must be used [20].

The intensity-dependent modification of the refractive index arising from the third-order susceptibility is known as the optical Kerr effect, and the parameter n_2 is commonly used as a figure of merit for comparing third-order nonlinear materials.

1.2.5 Limitations of Standard Dielectrics: Low n_2

The magnitude of n_2 and $\chi^{(3)}$ strongly depends on the physical process involved in modifying the refractive index. Table 1.1 summarizes the most common processes, along with the representative values of n_2 , $\chi^{(3)}$, and corresponding response times of the material, for linearly polarized light [6].

The nonlinear responses associated with electric polarization are extremely fast, with response times on the order of femtoseconds, but they typically exhibit relatively small nonlinearities ($n_2 \approx 10^{-16} \text{ cm}^2/\text{W}$). Here, the nonlinear response arises from the response of the bound electrons to the applied optical field. This process is predominant in all standard dielectrics. In contrast, thermal processes can lead to large nonlinearities ($n_2 \approx 10^{-6} \text{ cm}^2/\text{W}$), but at the cost of slow response times. The change in refractive index arises from local heating of the material caused by the absorption of incident laser power. This apparent trade-off between nonlinear

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Table 1.1: Typical values of the nonlinear refractive index, third-order nonlinear susceptibility, and material response times based on the physical processes involved [6].

Mechanism	n_2 (cm ² /W)	$\chi_{1111}^{(3)}$ (m ² /V ²)	Response time (s)
Electronic polarization	10^{-16}	10^{-22}	10^{-15}
Molecular orientation	10^{-14}	10^{-20}	10^{-12}
Electrostriction	10^{-14}	10^{-20}	10^{-9}
Saturated atomic absorption	10^{-10}	10^{-16}	10^{-8}
Thermal effects	10^{-6}	10^{-12}	10^{-3}

strength and material response time is a common limitation of conventional nonlinear materials.

In a bulk nonlinear material, the temporal modulation of the refractive index leads to the accumulation of the nonlinear phase shift as it propagates. For the propagation length of L , the nonlinear phase accumulated is given by

$$\Delta\phi = \frac{2\pi}{\lambda}\Delta nL, \quad (1.23)$$

where λ is the vacuum wavelength. To achieve a significant nonlinear phase shift, we require either high Δn or long interaction lengths. Long interaction lengths make material systems less compatible for the miniaturization of nanophotonic systems. Additionally, phase matching prevents arbitrarily long propagation lengths. For instance, in four-wave mixing (FWM), phase matching is essential for efficient frequency conversion. The phase matching coming from momentum conservation is given as

$$\Delta k = k_1 + k_2 - k_3 - k_4 = 0, \quad (1.24)$$

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where k_i are the wavevectors of the participating waves. Maximizing the change in refractive index, $\Delta n = n_2 I$, is not only limited by the weak nonlinear refractive index but also by the damage threshold or saturation behavior of the material [6, 10].

In integrated photonic platforms, to overcome the weak nonlinear response of traditional dielectrics and semiconductors, the effective interaction length is increased by using long waveguides or by enhancing the fields in high- Q ring resonators [21–23]. These approaches can substantially enhance nonlinear interactions, but they often require careful dispersion engineering and relatively complex fabrication to maintain phase matching and strong confinement.

An alternative approach is to use material platforms that provide large refractive-index modulation preferably on sub-picosecond time scales while remaining compatible with nanoscale integration and complementary metal–oxide–semiconductor (CMOS) fabrication. Materials operating in the epsilon-near-zero (ENZ) regime provide such a possibility and are discussed in the following section.

1.3 Epsilon-near-zero materials

In epsilon-near-zero (ENZ) materials, the real part of the permittivity approaches zero at a particular optical frequency [10, 12, 24]. Although the real part of the permittivity approaches zero, the imaginary part of the permittivity is not necessarily zero in ENZ materials. The ENZ condition naturally occurs in materials systems near their optical resonances. For instance, in metals, the ENZ condition occurs in the ultraviolet region of the electromagnetic spectrum,

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where they exhibit bulk plasma resonance. However, in the context of integrated nanophotonics, transparent conducting oxides (TCOs) exhibit ENZ behavior in the near infrared region [8, 10, 12]. In this section, we will elaborate on the optical response of TCOs in the ENZ region and the associated field enhancements.

1.3.1 Optical response of TCOs in ENZ region

Transparent conducting oxides are degenerately doped wide-bandgap semiconductors. Materials such as indium oxide, zinc oxide, or cadmium oxide are optically transparent in the visible spectrum due to their wide band gaps and become electrically conductive upon degenerate doping. TCOs, such as indium tin oxide (ITO) and aluminum zinc oxide (AZO), have been widely used in applications such as photovoltaics, touchscreens, flat-panel displays, and light-emitting devices.

The number of free carriers in TCOs determines the spectral region where the real part of the permittivity transitions from positive (dielectric-like behavior) to negative (metal-like behavior) [25]. The spectral region where $\text{Re}(\epsilon)$ approaches zero (often defined as $|\text{Re}(\epsilon)| < 1$) is referred to as the ENZ region. Although the typical free-carrier density is lower than that of noble metals, it can be easily manipulated via doping during TCO deposition. As a result, the zero crossing of permittivity, the ENZ region, can be spectrally tuned across the telecommunication region (near-IR to mid-IR).

Figure. 1.2 shows the dispersion of real and imaginary parts of the permittivity as well as the real part of the refractive index for a typical ENZ material. The ENZ spectral region lies in the near-infrared. In the region where the $\text{Re}(\epsilon) = 0$, the real part of refractive index depends mainly

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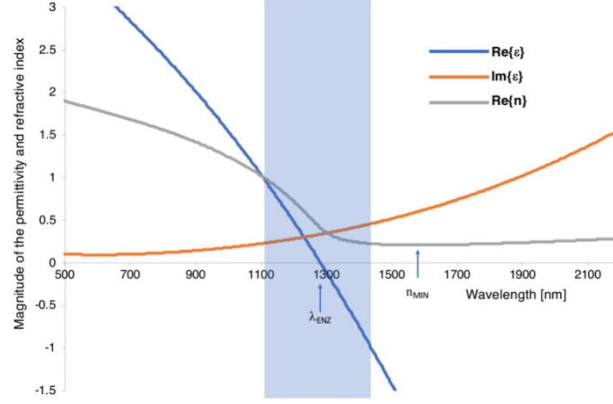


Figure 1.2: Dispersion of a typical ENZ material showing real and imaginary components of dielectric permittivity along with the real component of linear refractive index. Reproduced from [26] under the Creative Commons CC BY license.

on the $\text{Im}(\epsilon)$ as

$$\text{Re}(n) = \sqrt{\frac{|\text{Im}(\epsilon)|}{2}}. \quad (1.25)$$

This shows that near the ENZ region, the real part of the refractive index becomes small. Since $n_2 \propto 1/(n_0 \text{Re}(n_0))$ (Eq. 1.21), this can, in principle, lead to an enhanced effective nonlinear response.

The presence of free carriers dominates the optical response of TCOs in the near-infrared region. In this regime, we treat TCOs as a free-electron gas and use the Drude model to describe their linear optical properties. The Drude model treats the free carriers in a metal or doped semiconductor as a gas of independent electrons. This electron gas can be displaced by the optical field and oscillates with a characteristic frequency known as the plasma frequency (Eq. 1.26).

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$$\omega_p = \sqrt{\frac{Ne^2}{m_e^* \epsilon_0}}, \quad (1.26)$$

where N is the carrier density and m^* is the effective mass of the charge carriers. Under an applied laser field $\tilde{E}(t) = E_0 e^{-i\omega t} + \text{c.c.}$, the resulting frequency-dependent permittivity is given by the Drude model [6, 27] as

$$\epsilon_r(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \quad (1.27)$$

where ϵ_∞ represents the background permittivity associated with bound electrons (equal to 1 in the ideal free-electron limit), γ is the damping rate, and ω_p is the plasma frequency.

For a Drude material, the real part of the permittivity decreases with increasing wavelength. In the lossless limit, the zero-crossing occurs at $\omega = \omega_p / \sqrt{\epsilon_\infty}$. In the presence of damping, the permittivity remains complex, so even when $\text{Re}(\epsilon)$ approaches zero, $\text{Im}(\epsilon)$ remains finite. Since the plasma frequency depends on the carrier concentration, the ENZ crossing can be tuned by varying the doping level. As a result, TCOs allow the ENZ region to be tuned anywhere across the near- to mid-infrared spectral range.

In the following section, we examine how this ENZ condition influences the nonlinear optical response.

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1.3.2 Field enhancement in the ENZ region

As discussed in Sec. 1.2.5, strong nonlinear optical effects can arise from large intrinsic nonlinearities, increased interaction length, or enhanced local electric fields. In subwavelength-thick films, increasing the interaction length is not a practical route to stronger nonlinear interactions. Instead, enhanced local electric fields provide a mechanism to strengthen the nonlinear response. In this subsection, we explain why the ENZ condition leads to electric field enhancement inside the material.

The field enhancements in ENZ materials originate from electromagnetic boundary conditions. Consider a p-polarized plane wave incident from air onto a medium with permittivity ε at an angle θ . Let E_0 denote the amplitude of the incident electric field in air. The electric field can be decomposed into components parallel and perpendicular to the interface.

According to Maxwell's equations, at the interface between two media, the tangential component of the electric field is continuous,

$$E_{\parallel} = E_0 \cos \theta, \quad (1.28)$$

In the absence of surface charges, ensuring the continuity of the normal component of the electric displacement field, $\mathbf{D} = \varepsilon \mathbf{E}$, leads to

$$\varepsilon E_{\perp} = E_0 \sin \theta. \quad (1.29)$$

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These relations show that the normal component of the electric field inside the medium scales as

$$E_{\perp} = \frac{E_0 \sin \theta}{\varepsilon}. \quad (1.30)$$

The total field magnitude inside the medium is therefore given by

$$|E| = |E_0| \sqrt{\cos^2 \theta + \frac{\sin^2 \theta}{|\varepsilon|^2}}. \quad (1.31)$$

Near the ENZ condition, where $\text{Re}(\varepsilon) \rightarrow 0$, the normal component dominates, and the field inside the material scales approximately as

$$|E| \sim \frac{|E_0| \sin \theta}{|\varepsilon|}. \quad (1.32)$$

Thus, even for moderate incident fields, the internal electric field can become significantly enhanced. This enhancement is strongest at oblique incidence, where the normal component of the electric field is maximized. The resulting large local fields play a central role in enhancing nonlinear optical processes in ENZ materials. The spatial distribution of this enhanced field in thin films is discussed in the following subsection (see Fig. 1.7c).

1.4 Optical nonlinearities in ENZ materials

In the previous sections, we introduced epsilon-near-zero (ENZ) materials and showed that transparent conducting oxides (TCOs) exhibit ENZ behavior in the near-infrared spectral region

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[8, 10]. We discussed the consequences of low permittivity near the ENZ wavelength: (i) a small linear refractive index, and (ii) significant electric-field enhancement inside the ENZ material due to electromagnetic boundary conditions. These two factors suggest that ENZ thin films may support unusually large nonlinear optical responses, potentially beyond the validity of the standard perturbative Kerr approximation (Eq. 1.20). In the following sections, we examine the experimental observations of enhanced nonlinear response in subwavelength ENZ films.

Recently, subwavelength TCOs, such as degenerately doped ITO and AZO, have demonstrated significant nonlinear responses [8, 9]. In this section, we focus primarily on ITO, the primary material platform in this thesis, and review the experimental observations that motivate the remainder of this work.

The permittivity dispersion of thin ITO films is well described by the Drude model introduced in the previous section. For a 310 nm ITO film reported in [8], spectroscopic ellipsometry measurements agree closely with the Drude fit, as shown in Fig. 1.3. The epsilon-near-zero wavelength occurs at $\lambda_{\text{ZE}} = 1240$ nm, with $\varepsilon_{\infty} = 3.8055$, $\omega_p = 2\pi \times 473$ THz, and a damping rate of $\gamma = 0.0468\omega_p$.

At the ENZ wavelength, the imaginary part of the permittivity is $\varepsilon'' \approx 0.3$. Using Eq. 1.21, the corresponding linear refractive index is approximately $n_0 \approx 0.4$. The low refractive index of ITO in the ENZ region has two important consequences: an enhanced nonlinear refractive index coefficient, which scales inversely with n_0^2 , and strong electric-field enhancement within the film due to boundary conditions.

These properties have led to extensive experimental investigation of the nonlinear optical response

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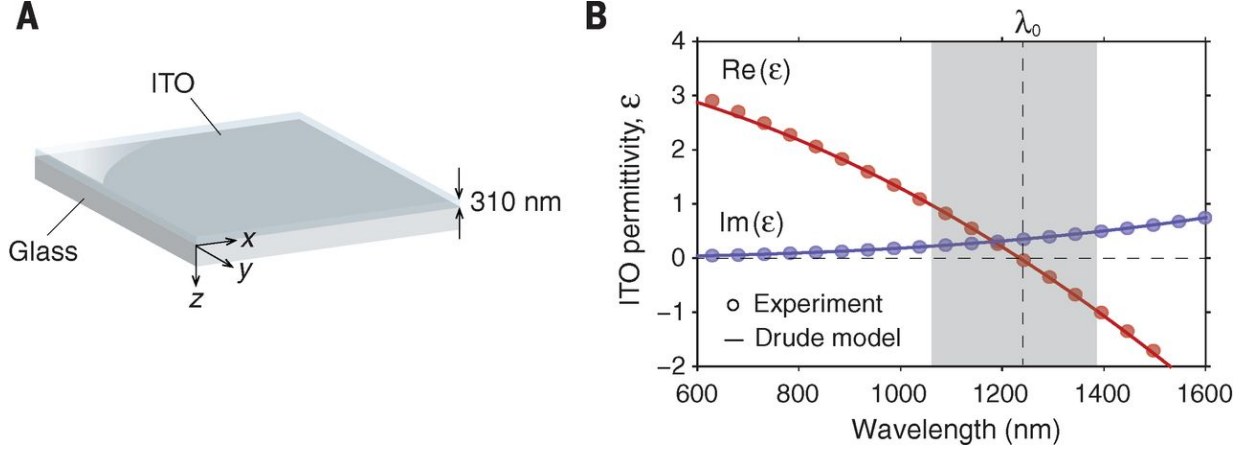


Figure 1.3: **Drude response of 310 nm ITO.** **a**, Schematic showing ITO film on a glass substrate, **b**, Linear relative permittivity measured via spectroscopic ellipsometry (dots) along with the Drude model fit (lines). From [8]. Reprinted with permission from AAAS.

of TCOs in the ENZ region. The next subsection presents the experimentally observed nonlinear response of ITO, followed by a discussion of the physical mechanisms responsible for these nonlinearities.

1.4.1 Large refractive index changes and ultrafast response in ENZ materials

Alam et al. [8] demonstrated a large and intensity-dependent refractive index in the ENZ region of a 310 nm ITO film. The real part of the permittivity crosses zero near 1240 nm. The effective nonlinear refractive index and nonlinear absorption coefficient, measured using the Z-scan technique, are shown in Fig. 1.4 for various angles of incidence.

At normal incidence in the ENZ region, the $n_{2(\text{eff})}$ and the $\beta_{(\text{eff})}$ are enhanced by approximately

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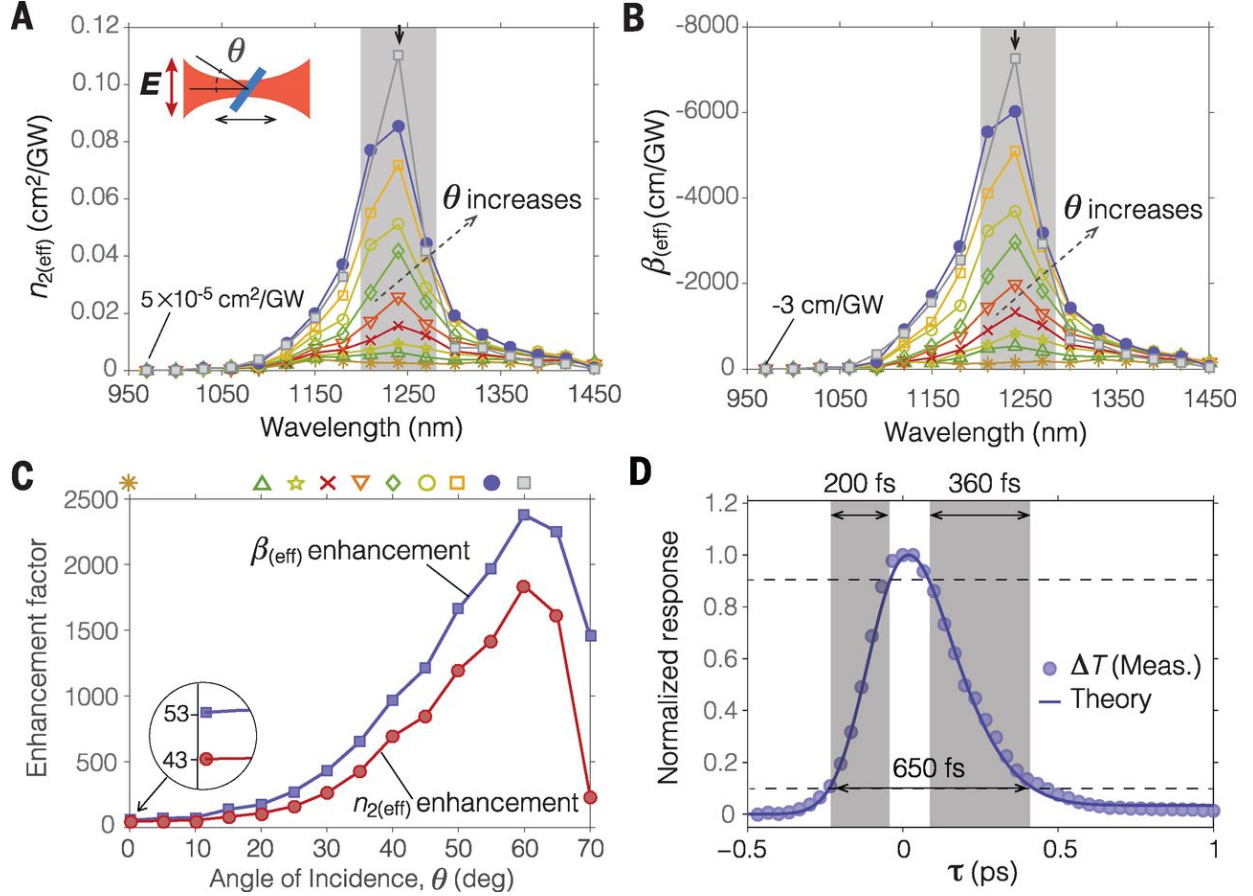


Figure 1.4: **Nonlinear optical response of a 310-nm-thick ITO film.** **a**, Effective nonlinear refractive index $n_{2(\text{eff})}$ and **b**, effective nonlinear absorption coefficient $\beta_{(\text{eff})}$ measured as functions of wavelength for different angles of incidence using the Z-scan technique. **c**, Corresponding enhancement factors at the ENZ wavelength relative to their values at 970 nm. **d**, Normalized transient change in probe transmission measured in a degenerate pump–probe experiment, showing sub-picosecond temporal dynamics. Adapted from [8]. Reprinted with permission from AAAS.

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43 and 53 times, respectively, compared to their values at a shorter wavelength (970 nm). When measured at oblique incidence, the enhancement increases dramatically, by factors of 1837 and 2377, respectively. This additional increase arises from electric-field enhancement associated with electromagnetic boundary conditions at an oblique angle of incidence.

Pump–probe measurements further revealed the ultrafast temporal dynamics of the nonlinear response [28, 29]. A strong pump pulse induces the nonlinear response, while a weak probe measures the resulting transient transmission. The nonlinear response exhibits a rise time of approximately 200 fs and a recovery time of 360 fs (Fig. 1.4d), confirming that the mechanism operates on sub-picosecond time scales.

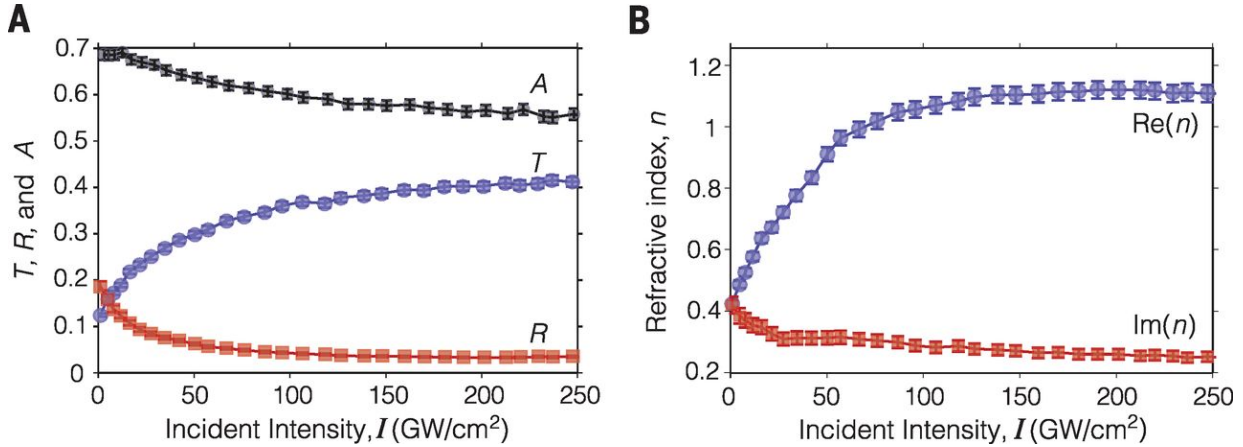


Figure 1.5: **Intensity-dependent optical response of a 310-nm-thick ITO film.** **a**, Transmittance (T), reflectance (R), and absorptance (A) as functions of incident intensity at the ENZ wavelength for $\theta = 30^\circ$. **b**, Corresponding complex refractive index extracted using a transfer-matrix method. Adapted from [8]. Reprinted with permission from AAAS.

Fig. 1.5 shows that the refractive index changes from $n_0 = 0.4$ to $n = 1.1$, indicating that the change

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in refractive index, $\Delta n = 0.7$ does not satisfy the perturbative approximation, $|2n_2 I / n_0| \ll 1$ from Eq. 1.20. The nonlinear response must instead be described through the full intensity-dependent modification of the permittivity governed by carrier dynamics. The physical mechanisms underlying this behavior are discussed in the following subsection.

1.4.2 Physical mechanisms of the large nonlinear response

The unusually large and ultrafast nonlinear response observed in ITO in the ENZ region is explained by examining the underlying carrier dynamics.

Third-order nonlinearities can, in general, be classified as either fast or slow. Fast nonlinearities are associated with virtual processes and are near-instantaneous [30]. In contrast, slow nonlinearities arise from real excitations and typically occur on ps–ns time scales. The bound-electron nonlinearities described in Table 1.1 are associated with virtual processes, while thermal nonlinearities are related to real excitations.

Figure 1.6 illustrates both the fast and slow intraband nonlinearities in the nonparabolic conduction band [30–32]. The large nonlinear response in ITO is associated with free-carrier dynamics, in particular the redistribution of carriers within a nonparabolic conduction band, as illustrated on the right side of Fig. 1.6. Under intense optical excitation, intraband (free-carrier) absorption rapidly increases the electron temperature and redistributes carriers in the conduction band. In ENZ materials, due to the nonparabolicity of the conduction band, the carrier effective mass increases. According to the Drude model described in Eq. 1.27, as the carrier effective mass increases, the plasma frequency decreases and redshifts to lower frequencies.

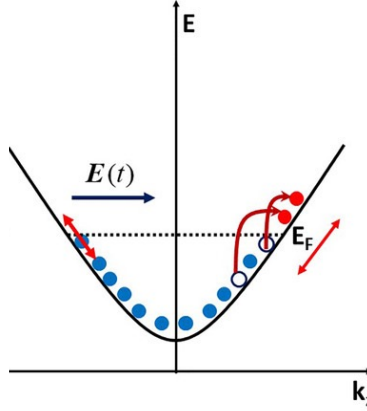


Figure 1.6: **Carrier redistribution in a nonparabolic conduction band under optical excitation.** Schematic of the conduction band energy E versus wavevector k_z . Under intense optical excitation $E(t)$, carriers are heated and redistributed to higher energies above the Fermi level E_F . Due to the nonparabolicity of the conduction band, this redistribution increases the carrier effective mass. The resulting modification of the plasma frequency governs the intensity-dependent permittivity shift in ENZ materials. Adapted from [30] under the Creative Commons CC BY license.

This intensity-driven shift of ω_p modifies the permittivity dispersion $\varepsilon(\omega)$, effectively displacing the ENZ wavelength (Fig. 1.7(a)). Because the refractive index variation is largest near the zero-permittivity wavelength, even a slight shift in plasma frequency produces a substantial change in refractive index (Fig. 1.7(b)) — the nonlinear index modulation, therefore, peaks near the ENZ condition. In addition, the boundary-condition-enabled field enhancement at oblique incidence further amplifies this effect (Fig. 1.7(c)), leading to the large effective nonlinear coefficients discussed in the previous subsection.

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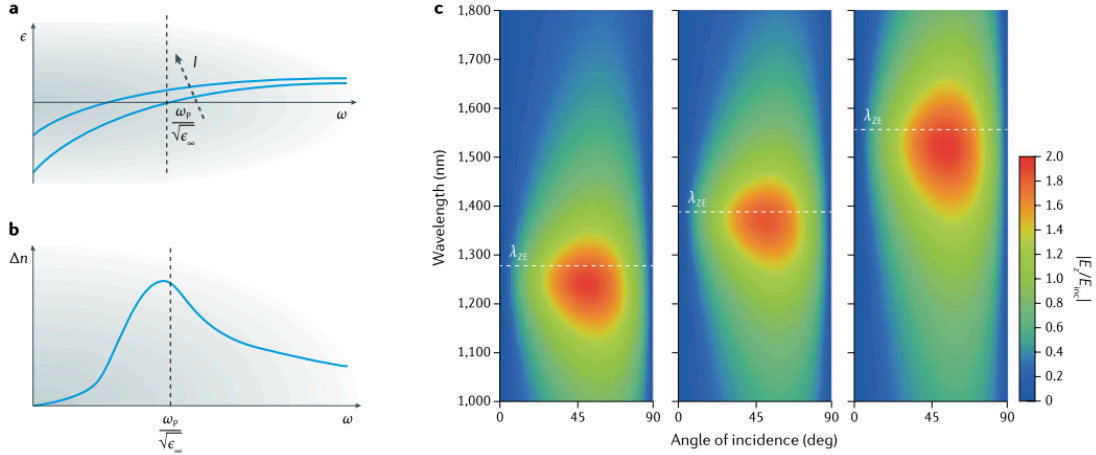


Figure 1.7: **Nonlinear mechanisms and field enhancement in ITO.** (a) Intensity-induced shift of the plasma frequency ω_p modifies the permittivity dispersion $\epsilon(\omega)$ and shifts the ENZ wavelength. (b) The corresponding change in refractive index Δn peaks near the zero-permittivity wavelength. (c) Calculated electric-field enhancement $|E_z/E_{inc}|$ for p-polarized light at the air/ITO interface for a 37-nm-thick ITO film as a function of wavelength and angle of incidence, showing maximum enhancement near the ENZ wavelength and at oblique incidence. The three panels illustrate the spectral shift of the maximum field enhancement for different intensities. Panels (a,b) reproduced from [10]. Panel (c) adapted from [17] with permission from the Optical Society of America.

Furthermore, this excited carrier distribution relaxes as the hot carriers cool. Therefore, it is similar to "slow" nonlinearities in conventional dielectrics, since the relaxation is determined by hot-carrier lifetimes [30–32]. However, in ITO, the electron–lattice relaxation time is shorter than one picosecond, compared to nanoseconds in typical dielectrics. As a result, the free-carrier nonlinearity in ITO remains sub-picosecond and therefore ultrafast.

The nonlinear response of ITO in the ENZ region can therefore be interpreted as an intensity-

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driven, hot-carrier-induced shift of the plasma frequency. The large magnitude of the change in refractive index in ITO is due to a combination of effects: (i) low refractive index at the plasma frequency, (ii) boundary-condition-enabled field enhancement, and (iii) optical-pumping-induced plasma frequency shift due to nonparabolicity of the conduction band. The temporal dynamics are governed by carrier relaxation in ITO, which occurs on sub-picosecond time scales. A standard approach to modeling these nonlinearities is the two-temperature model [33, 34], which is beyond the scope of this thesis.

1.4.3 Adiabatic frequency conversion

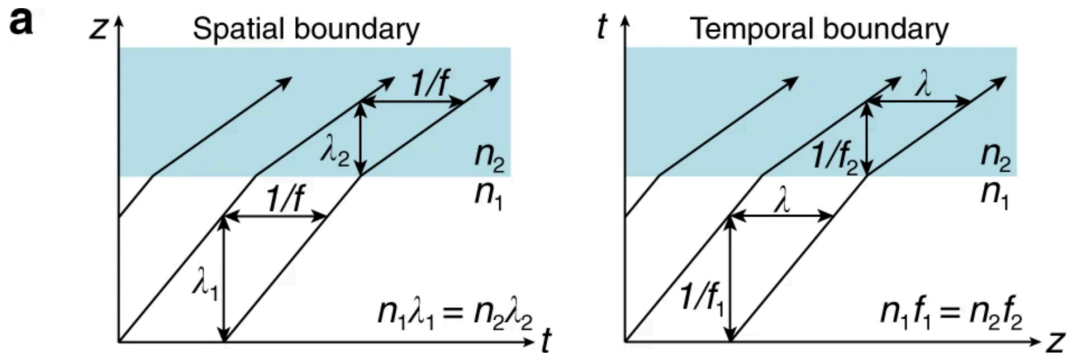


Figure 1.8: **Spatial versus temporal refraction.** At a spatial boundary, the frequency is conserved while the wavevector changes, leading to $n_1\lambda_1 = n_2\lambda_2$. At a temporal boundary, the wavevector is conserved while the frequency changes, leading to $n_1f_1 = n_2f_2$. Reproduced from [13] under the Creative Commons CC BY 4.0 license.

The large and ultrafast temporal variation of the refractive index modulation in ITO leads to significant time refraction [35, 36]. Our group demonstrated a broadband frequency shift of 14.9

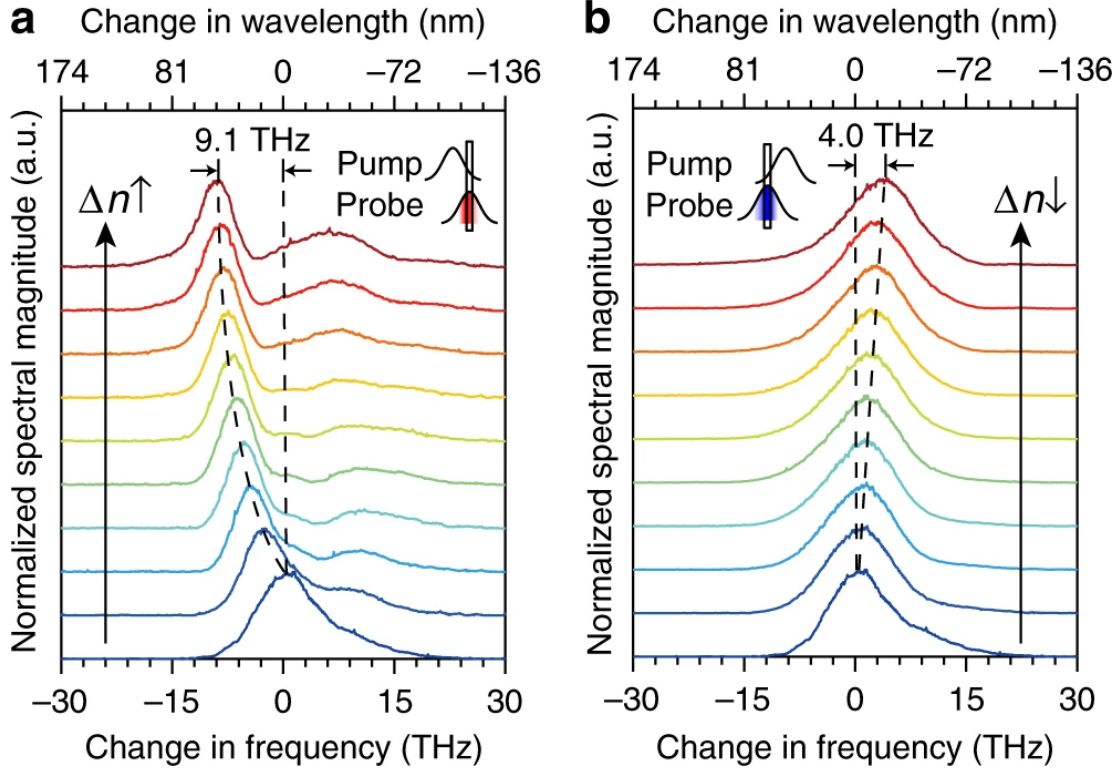


Figure 1.9: **Frequency shifts induced by time refraction in ENZ ITO.** Measured probe spectra showing redshift for **a**, $\Delta n > 0$, and **b**, blueshift for $\Delta n < 0$ in an optically pumped ITO film. Reproduced from [13] under the Creative Commons CC BY 4.0 license.

THz in the ENZ spectral region of 620 nm ITO [13], corresponding to approximately a 76 nm wavelength shift around the ENZ crossover wavelength of 1240 nm.

Time refraction can be understood by analogy with spatial refraction and Snell's law. As with spatial variation in refractive index, temporal variation in refractive index leads to time refraction. In the spatial scenario, the wavevector changes and the frequency is conserved; by contrast, when the refractive index varies in time, meaning at $t = t_1$, the index changes from n_1 to n_2 , as a

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consequence of the broken time-translation symmetry, the frequency of the light changes, keeping the wavevector unchanged (Fig. 1.8). Using the relation $c/f = n\lambda$, the change in frequency can be expressed as $n_1 f_1 = n_2 f_2 = (n_1 + \Delta n)(f_1 + \Delta f)$, where $\Delta f = f_2 - f_1$ is the change in the frequency of light after it encounters the temporal boundary; $\Delta n = n_2 - n_1$ is the change in the refractive index; and c is the speed of light in vacuum. This leads to $\Delta f = -\Delta n f_1 / (n_1 + \Delta n)$.

Physically, while a spatial interface breaks translation symmetry in space and conserves frequency, a temporal interface breaks translation symmetry in time and conserves momentum (k). This relation shows that a frequency shift will be red (blue) if the change in index Δn is positive (negative). In ITO, we see that as Δn increases, the frequency redshifts by 9.1 THz, and as Δn decreases, the frequency blueshifts by 4.0 THz, as shown in Fig. 1.9.

The large and ultrafast nonlinear response of ITO, as well as time refraction, form the basis of the experimental investigations presented in subsequent chapters.

1.4.4 ENZ and Berreman modes in ultrathin ENZ films

In the previous sections, we discussed how the vanishing permittivity of ENZ materials enables electric-field enhancement at boundaries and a large nonlinear optical response in subwavelength-thick ITO films. In this section, we examine how the electromagnetic modes supported by the structure evolve as the film thickness is reduced well below the optical skin depth, approaching the ultrathin-film limit.

In a bulk metal described by the Drude model, electromagnetic waves propagate only when the excitation frequency exceeds the plasma frequency ω_p . At a metal–dielectric interface, coupling

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between the electromagnetic field and collective oscillations of free electrons gives rise to surface plasmon polaritons (SPPs). These modes are transverse-magnetic (TM) polarized surface waves localized at the interface and characterized by an in-plane wavevector that exceeds the free-space wavenumber $k_0 = \omega/c$, indicating that they are non-radiative and bound to the interface [27, 37]. In this conventional treatment, both media are assumed to be semi-infinite.

When the metal thickness becomes comparable to the optical skin depth, the electromagnetic modes are modified by the presence of the second interface. We therefore consider the general case of a three-layer system consisting of a thin metallic film (ϵ_2) sandwiched between two dielectric media (ϵ_1 and ϵ_3), as illustrated in Fig. 1.10. The film has thickness d and the modes propagate along the interface with in-plane wavevector $k_{\parallel}$.

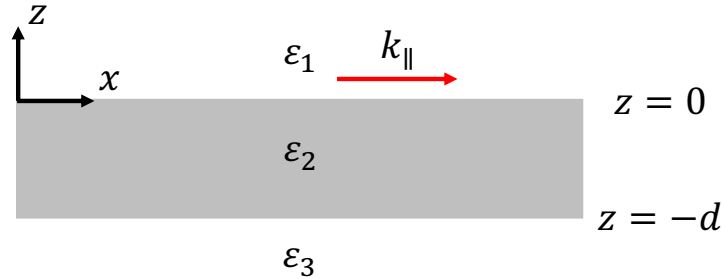


Figure 1.10: **Three-layer geometry used to calculate thin-film plasmon modes.** A metallic layer with permittivity ϵ_2 and thickness d is sandwiched between two semi-infinite dielectric regions with permittivities ϵ_1 and ϵ_3 . The electromagnetic modes propagate along the interface with in-plane wavevector $k_{\parallel}$.

The electromagnetic eigenmodes of this structure can be obtained by solving Maxwell's equations subject to the boundary conditions at both interfaces. For TM polarization, the allowed modes

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satisfy the dispersion relation given by

$$1 + \frac{\varepsilon_1 k_{z3}}{\varepsilon_3 k_{z1}} = i \tan(k_{z2} d) \left(\frac{\varepsilon_2 k_{z3}}{\varepsilon_3 k_{z2}} + \frac{\varepsilon_1 k_{z2}}{\varepsilon_2 k_{z1}} \right), \quad (1.33)$$

where

$$k_{zi}^2 = \varepsilon_i k_0^2 - k_{\parallel}^2, \quad k_0 = \frac{\omega}{c}, \quad (1.34)$$

and $i = 1, 2, 3$ correspond to the superstrate, thin film, and substrate, respectively. The metal layer is described using the Drude model as

$$\varepsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \quad (1.35)$$

while for simplicity the surrounding media are taken to be free space ($\varepsilon_1 = \varepsilon_3 = 1$).

The solutions of Eq. 1.33 depend strongly on the film thickness. Figure 1.11 shows the calculated dispersion relation for ENZ films with thicknesses of 2 nm, 20 nm, and 150 nm.

When the film thickness is relatively large, the dispersion resembles that of a conventional surface plasmon polariton supported at a single metal–dielectric interface. As the thickness decreases, the modes supported at the two interfaces begin to interact. This interaction leads to modified dispersion branches commonly referred to as long-range and short-range plasmon modes [38, 39]. In the ultrathin limit, the dispersion becomes nearly flat near the frequency at which the permittivity approaches zero, and the associated longitudinal electric field is strongly enhanced inside the film.

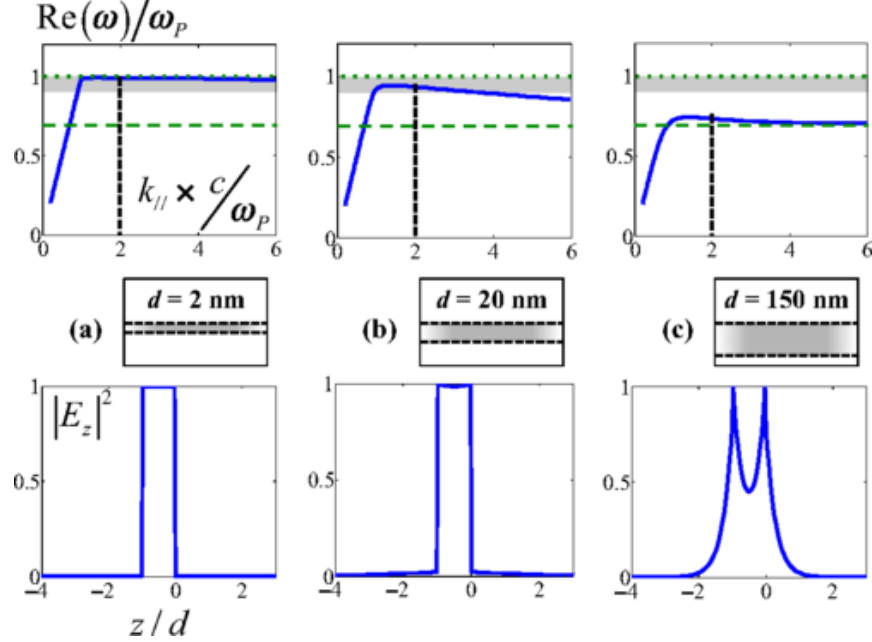


Figure 1.11: Thickness-dependent dispersion and field enhancement in ENZ thin films. Top row: Normalized dispersion relation $\text{Re}(\omega)/\omega_p$ as a function of the normalized in-plane wavevector $k_{||}c/\omega_p$ for film thicknesses (a) $d = 2$ nm, (b) $d = 20$ nm, and (c) $d = 150$ nm. The shaded gray region indicates the ENZ mode validity range, and the dashed vertical line denotes the fixed wavevector at which the field profiles are evaluated. As the film thickness decreases, the dispersion evolves toward a nearly flat branch near the ENZ frequency. Bottom row: corresponding longitudinal electric-field intensity $|E_z|^2$ across the film thickness (plotted as a function of z/d). In the ultrathin limit, the field becomes nearly uniform inside the film, whereas thicker films exhibit more localized field distributions. Adapted from [38].

A key feature of ENZ materials is the appearance of longitudinal resonances near the ENZ frequency. These modes can be classified into two types depending on their position relative

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to the light line, as illustrated in Fig. 1.12[12]. The branch located to the left of the light line corresponds to the Ferrell–Berreman mode [10, 40]. This mode is radiative and can therefore be excited directly from free space using p-polarized light at oblique incidence. Experimentally, it appears as a strong absorption resonance near the ENZ wavelength.

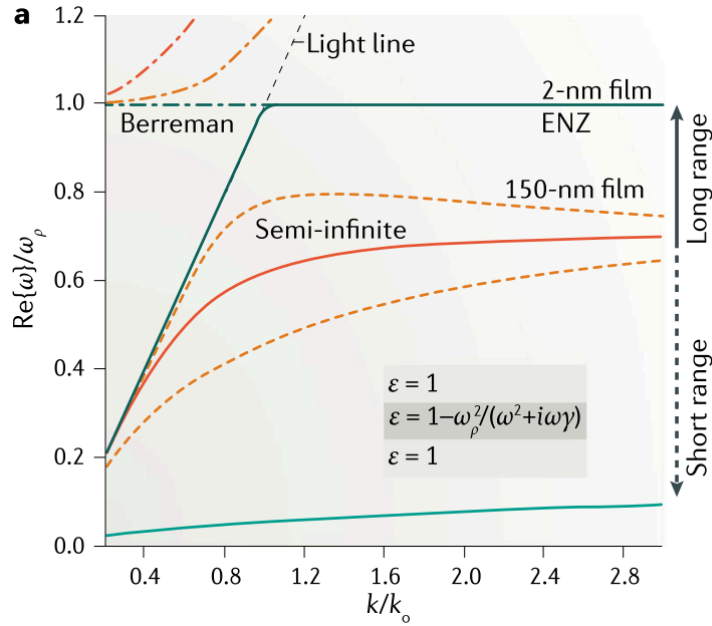


Figure 1.12: **Radiative and confined modes in ENZ thin films.** The Ferrell–Berreman mode appears to the left of the light line and can couple directly to free-space radiation. The confined ENZ mode lies to the right of the light line and therefore requires additional in-plane momentum for excitation. Both modes occur near the ENZ frequency where $\text{Re}(\varepsilon) = 0$. The dispersion is shown in terms of $\text{Re}(\omega)$ to indicate the observable frequency in the presence of material losses. The inset illustrates a dielectric–ENZ–dielectric structure, where the ENZ layer is described by a Drude permittivity $\varepsilon = 1 - \omega_p^2/(\omega^2 + i\omega\gamma)$ and is surrounded by dielectric media with $\varepsilon = 1$. Reproduced from [12].

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In contrast, the branch located to the right of the light line corresponds to a confined ENZ mode. Because this mode possesses an in-plane wavevector larger than that of free-space radiation, it cannot be excited directly from free space due to momentum mismatch. Nevertheless, it supports strong longitudinal electric fields within the film and therefore provides an efficient mechanism for enhancing light–matter interactions in ultrathin ENZ layers.

Both modes occur near the ENZ frequency and can lead to substantial field enhancement in thin ENZ films. In this thesis, we exploit these two types of modes in different device architectures. In Chapter 5, we use the radiative Berreman mode in ITO–Si bilayers to generate asymmetric field enhancement and nonlinear transmission. In Chapter 6, we access the confined ENZ mode using plasmonic nanoantennas patterned on ultrathin ITO films. In this case, the localized surface plasmon resonance of the nanoantennas provides the additional in-plane momentum required to couple incident light into the ENZ mode of the film.

Plasmonic metasurfaces, therefore, provide an effective platform for coupling free-space radiation to otherwise inaccessible ENZ modes while simultaneously enhancing the local electromagnetic fields [26, 41]. In the following section, we describe the fabrication of plasmonic metasurfaces used throughout this thesis and briefly review several metasurface geometries explored during the course of this work.

1.5 Metasurface design and fabrication

Plasmonic (or dielectric) metasurfaces patterned on ultrathin ENZ materials enhance the local electromagnetic fields through the resonant response of the nanoantennas. In addition, the metasurface provides the required momentum matching to couple incident light from free space to the ENZ modes supported by the ultrathin ENZ films. This coupling becomes efficient when the nanoantenna resonances are designed to occur near the ENZ wavelength, enabling strong coupling between the nanoantenna resonance and the ENZ modes.

As a result, metasurfaces on ENZ films provide a useful platform for enhanced light–matter interaction for a broad range of nonlinear phenomena in ultrathin films [11, 26, 41], including enhanced harmonic generation, four-wave mixing [15], ultrafast switching [42], adiabatic frequency conversion [14], quantum light generation [43], and absorption control [44].

Beyond the specific devices presented in Chapters 2–6, a significant part of my PhD work involved the design, fabrication, and characterization of a variety of metasurface platforms as ongoing and exploratory studies. Although these samples are not the primary focus of this dissertation, they reflect the broader experimental infrastructure and fabrication expertise developed during the PhD.

1.5.1 Metasurface platforms fabricated and characterized during the PhD

An SEM image of the plasmonic metasurfaces fabricated during my PhD is shown in Fig. 1.13.

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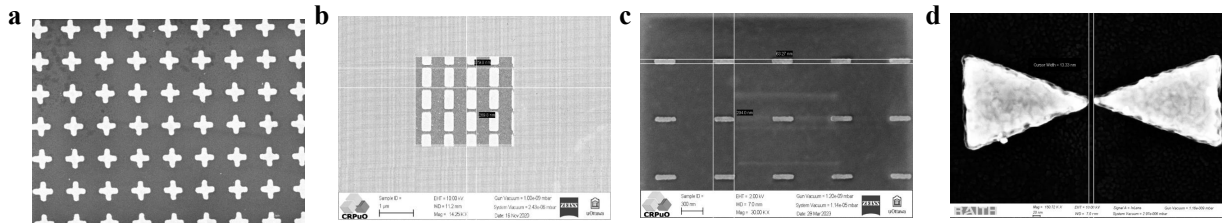


Figure 1.13: **Plasmonic metasurfaces fabricated.** **a**, Cross-shaped Au nanoantennas on 23 nm ITO. **b**, Rectangular Au nanoantennas on 23 nm ITO. **c**, Rectangular Au nanoantennas on lithium niobate. **d**, Bowtie Au nanoantennas on 23 nm ITO

1. **Gold nanoantennas on ITO:** Fabricated periodic arrays of Au nanoantennas (e.g., 30 nm thick rods, symmetric and asymmetric crosses) on ultrathin 23 nm ITO films to enhance local optical fields via coupling of the localized surface plasmon resonance mode (LSPR) of the nanoantenna to the ENZ mode of ITO. These metasurfaces were designed to explore coherent perfect absorption, ultrafast polarisation rotation, and suppression of structural birefringence. The CPA structures were fabricated with the intention of serving as an experimental follow-up to the work described in Chapter 6. The SEM images are shown in Fig. 1.13(a,b).
2. **ITO/Au bilayer structures:** Deposited 200 nm Au film on top of 23-nm and 310-nm ITO films to enhance the Berreman mode in ITO to study ultrafast all-optical switching. This project was initially pursued as a potential platform for strong nonlinear modulation, but was later set aside in favor of the more promising cavity-mode-based design described in the four-wave mixing and cavity dynamics chapters.
3. **Au nanoantennas on thin-film Lithium niobate:** Fabricated Au nanoantennas on top of

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a 700 μm -thick lithium niobate layer with the goal of enhancing spontaneous parametric down-conversion (SPDC) through plasmonic field confinement. This study was intended as a comparison to SPDC from dielectric metasurface patterned on LiNbO_3 metasurfaces ([45]). In practice, no measurable SPDC signal was observed, which was attributed to excessive absorption losses in the plasmonic structures. The SEM image is shown in Fig. 1.13(c).

4. **Au bowtie nanoantennas on ITO:** Fabricated Au bowtie nanoantennas with separations of approximately 13–20 nm between the antenna tips to achieve the strong local field enhancements required for strong coupling with quantum emitters. These structures were designed to maximize field confinement in the gap region. The SEM image is shown in Fig. 1.13(d). This project remains ongoing.
5. **Fourier-transform surface lattice resonance (FT-SLR) metasurfaces:** I also contributed to the fabrication and optical characterization of metasurfaces designed to support Fourier-transform surface lattice resonances [46]. My role primarily involved consultation during fabrication and performing linear optical characterization of the fabricated sample. The resulting study is included in the appendix.
6. **Dielectric Mie-resonant metasurfaces:** In addition to plasmonic metasurfaces, I was involved in the experimental characterization of dielectric metasurfaces supporting electric and magnetic dipole resonances (EDR and MDR). These structures exhibit strong coupling between the EDR and MDR modes and the ITO ENZ mode. These structures were also used to study nonlinear optical responses under pump–probe excitation. My contribution

1.5. *METASURFACE DESIGN AND FABRICATION*

included linear optical characterization of the fabricated sample and the construction of the experimental pump-probe setup for nonlinear optical measurements. The resulting work is included in the appendix of this thesis [47]. These structures also offer opportunities to explore Kerker-effect-based directional nonlinear responses, which remain an ongoing area of investigation.

1.5.2 Fabrication protocol and process flow

To fabricate the metasurfaces described in the previous section, a standard nanofabrication workflow comprising electron-beam lithography (EBL), thin-film deposition, and lift-off is used. The schematic of the process is shown in Fig. 1.14 and summarized below:

1. **Substrate preparation:** Thin films of ITO, fused silica, Lithium niobate, or Indium phosphide on glass substrates were used, depending on the device platform. Substrates were first cleaned with standard solvents (acetone, then isopropanol) and then baked. When necessary, oxygen plasma treatment was used to remove organic residues and promote resist adhesion. The schematic is shown in Fig. 1.14(a).
2. **Resist coating:** A bilayer PMMA resist stack was used as the electron-beam resist and was spin-coated, followed by a soft bake. The bilayer resist plays an important role in enabling reliable nanoscale metal lift-off. The two resist layers have different molecular weights, resulting in different sensitivities to the electron beam dose. During development, this leads to a slight undercut profile, which facilitates clean metal lift-off and prevents

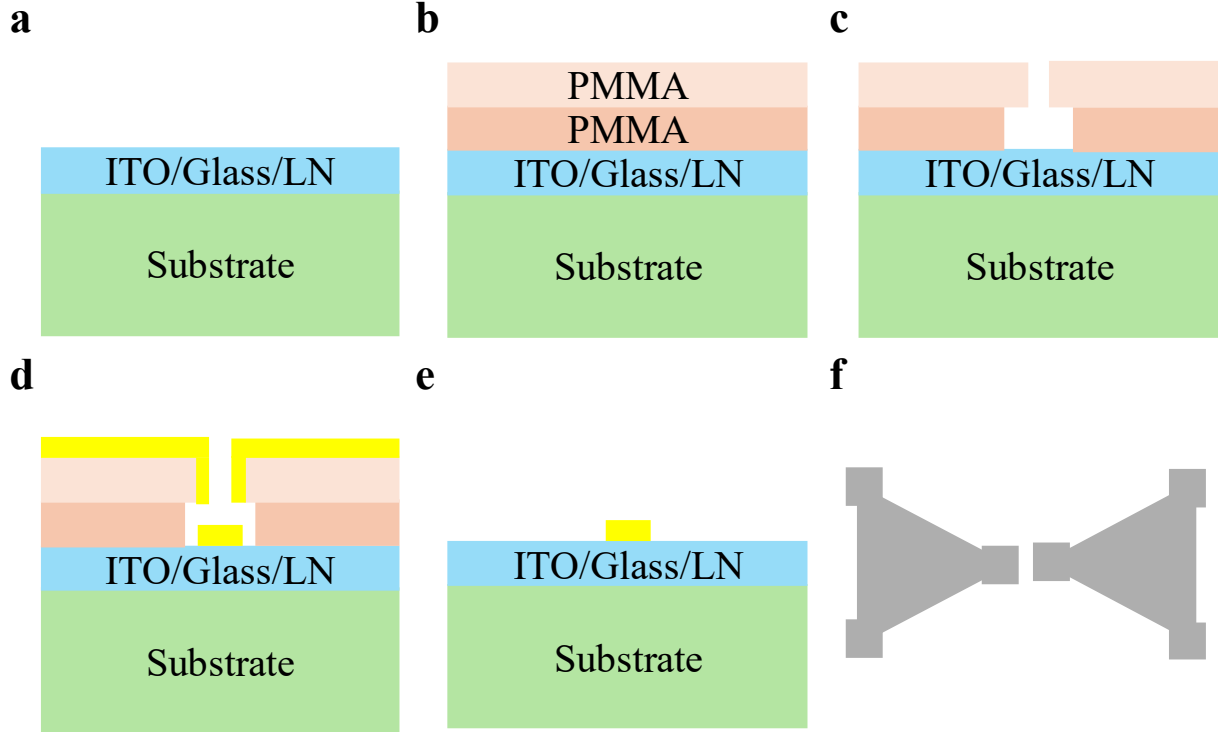


Figure 1.14: **Fabrication procedure of plasmonic metasurfaces**, Schematic showing ITO/fused silica/Lithium-niobate thin film on a glass substrate, **b**, bilayer resist deposition, **c**, schematic of resist after e-beam lithography, **d**, metal deposition, **e**, lift-off, **f**, Proximity error corrections serifs used in fabricating bowtie antennas with small gap

the formation of metal sidewalls that could short neighboring structures. The schematic is shown in Fig. 1.14(b).

3. **Patterning:** To achieve strong field enhancements and tune the localized surface plasmon resonance (LSPR) or surface lattice resonance (SLR) into the near-infrared region, nanoantennas with feature sizes of approximately 100–200 nm are typically required.

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Electron-beam lithography was therefore used to write the antenna geometries into the resist directly. The schematic is shown in Fig. 1.14(c).

4. **Development and metal deposition:** After electron-beam exposure, the resist was developed to reveal the patterned structure. Metal deposition was then performed by thermal evaporation, typically using Au with a thin adhesion layer of Ti or Cr, depending on the device's optical requirements. The schematic is shown in Fig. 1.14(d).
5. **Lift-off:** The lift-off process removes the remaining resist and excess metal, leaving behind only the patterned nanoantennas on the substrate. Care was taken during this step to avoid damaging the underlying ultrathin ENZ films. The schematic is shown in Fig. 1.14(e).
6. **Fabrication considerations for narrow bowtie gaps:** For bowtie antennas, the separation between the antenna tips plays a critical role since the local field enhancement scales strongly with both the sharpness of the tips and the proximity of the two antennas. Achieving gap sizes below ~ 20 nm is challenging, especially with 30 kV systems, due to proximity effects and larger beam spot sizes compared to 100 kV systems.

To overcome this limitation, proximity-effect correction techniques were implemented, including the use of serif structures that locally modify the electron-beam dose distribution [48]. By carefully tuning the exposure dose near the antenna tips, it was possible to compensate for proximity broadening and reliably fabricate gaps in the 13–20 nm range, even with a 30 keV electron-beam system. The schematic representation of structural proximity correction using serifs is shown in Fig. 1.14(f).

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7. **Fabrication characterization:** After the lift-off, the fabricated structures are first inspected using an optical microscope before moving to scanning electron microscopy (SEM) to verify the dimensions of the nanoantennas patterned. Linear optical measurements, such as transmission and reflection spectroscopy, were then performed prior to using the supercontinuum source in nonlinear optical experiments.

The fabrication process described in this section allowed us to test a range of metasurface geometries and device platforms. In practice, nanofabrication is always subject to tolerances, and devices rarely behave exactly as designed. For this reason, the structures presented in this thesis were developed through iteration, repeated cycles of design, fabrication, and optical measurements. Insights from the measurements were then used to refine the simulations and guide the development of the next generation of devices.

1.6 Structure of the Dissertation

The thesis consists of seven chapters, including an introduction and a conclusion. Chapters 2–6 are based on published and ongoing works and include contribution statements.

- Chapter 1 serves as an introduction to the dissertation.
- Chapter 2 is about parametric amplification of optical pulses in a time-varying nanomaterial via two-beam coupling, where we numerically demonstrate that in a strongly nonlinear medium, no initial frequency difference between the two interacting beams is required

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for the two beams to exchange energy. Furthermore, we experimentally and numerically demonstrate that the amplification of a weak probe beam is a quadratic function of the pump beam intensity and the nonlinear refractive index coefficient. We also show that two-beam coupling in a thin film of indium tin oxide in its epsilon-near-zero region results in energy transfer that is up to 10 orders of magnitude larger than in glass. Our results point to strategies for using time-varying nanomaterials to achieve broadband amplification via spatio-temporal modulation of the refractive index. *(This chapter is based on a manuscript published in Nano Letters)*

- Chapter 3 discusses the design of the ITO-based Gires–Tournois nanocavity. ITO acts as a nonlinear material and partial reflector, SiO_2 is used as the spacer, and Au as the perfect mirror. In this chapter, we show how the ITO nanocavity is engineered to exhibit a Brewster mode within the ITO, resulting in significant angle-dependent field enhancements. Furthermore, we experimentally and numerically demonstrate the spectral and temporal dynamics of the Brewster mode under optical pumping. The Brewster mode spectrally redshifts by approximately 170 nm with an on–off contrast of about 25 dB, demonstrating its potential for ultrafast optical switching. These angle-dependent field enhancements form the basis for the nonlinear processes explored in Chapter 4. *(This chapter is based on a manuscript prepared for submission.)*
- Chapter 4 discusses unity-order four-wave mixing (FWM) efficiencies. Here, we report a FWM conversion efficiency of 45% in a subwavelength-thick, easy-to-fabricate ITO-based Gires–Tournois nanocavity. We show that the angle-dependent field enhancement discussed

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in Chapter 3 directly leads to enhanced FWM efficiency, together with the strong nonlinear response of ITO in its epsilon-near-zero region. In addition, for a frequency-degenerate pump-signal case, we report conversion efficiencies of 10% for six-wave mixing and 2% for eight-wave mixing. *(This chapter is based on a manuscript prepared for submission.)*

- Chapter 5 discusses nonreciprocity in epsilon-near-zero dielectric bilayers, where we experimentally demonstrate a nonreciprocal transmission ratio of 2 in the ITO–Si bilayer system. We also show how the nonreciprocal transmission ratio varies spectrally and angularly in the ENZ region of ITO. *(This chapter is based on ongoing work currently being prepared for submission.)*
- Chapter 6 is about dynamic coherent perfect absorption in nonlinear metasurfaces, where we propose a tunable coherent perfect absorber based on plasmonic nanoantennas on top of ultrathin ITO films. Here, the metasurface is designed to couple the plasmonic resonance to the ENZ mode of ITO, and the coherent perfect absorption is achieved by controlling the relative phases of the input beams. We also demonstrate that the optical response of the nonlinear metasurface can be tuned from complete to partial absorption by varying the pump beam intensity. *(This chapter is based on a manuscript published in Optics Letters.)*
- Chapter 7 presents the conclusions and future directions.
- The appendices include two published collaborative works on plasmonic and dielectric metasurfaces that complement the main results of the thesis.

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Chapter 2

Parametric amplification of optical pulses through synthetic motion in a time-varying medium

Contribution Statement

I joined Professor Robert Boyd's group and began discussing the group's pioneering work on indium tin oxide (ITO) with Dr. Mohammad Zahirul Alam and later Dr. Yiyu Zhou. Under Dr. Alam's supervision, my colleague Theng-Loo Lim and I developed and carried out pump-probe measurements on ITO films. Our initial objective was to study four-wave mixing (FWM) in ITO using pump-probe measurements, during which we monitored the probe transmission as a function of pump-probe delay and the pump pulse intensity at the same frequency.

While performing these frequency-degenerate FWM measurements, Theng-Loo and I observed a nonlinear change in the probe transmission as a function of pump–probe delay that could not be explained solely by FWM. This observation led us to revisit the concept of two-beam coupling (TBC), as discussed in Prof. Boyd’s textbook *Nonlinear Optics*. However, several aspects of our observation differed from the traditional description of TBC. Conventionally, TBC considers two beams with slightly different frequencies whose interference creates a moving grating in the nonlinear material, leading to diffraction from one beam into the other. In the case of degenerate pulses, TBC is most commonly attributed to chirp in the pulses. Although our pump and probe pulses originated from the same source and were chirped, the magnitude of the TBC response we observed in ITO could not be explained solely by chirp.

Theng-Loo Lim, Dr. Alam, and I hypothesized that adiabatic frequency conversion (AFC) in ITO could introduce effective frequency differences between the pulses, thereby enabling coherent energy transfer. While Theng-Loo and I conducted experiments to isolate and quantify this effect, I performed numerical simulations in *Mathematica* under the guidance of Dr. Alam to support this hypothesis. Ultimately, we showed that when the refractive-index modulation becomes sufficiently large, the conventional linear TBC response due to chirp is dominated by a quadratic dependence on the pump intensity and the ITO’s nonlinear refractive index (n_2). This prediction agrees closely with our experimental observations.

My contributions to this work are summarized below:

1. Building, automating, and refining the experimental setup to quantify the TBC and AFC to isolate the TBC-induced change to probe transmission (primary contributor alongside

Theng-Loo Lim, with guidance from Dr. Mohammad Zahirul Alam and consultation with co-authors).

2. Performing the experiments and collecting the data (primary contributor alongside Theng-Loo Lim).
3. Numerical modeling and simulations in *Mathematica* to explain the observed behavior (primary contributor, with guidance from Dr. Mohammad Zahirul Alam).
4. Preparing the first draft of the manuscript (primary contributor alongside Theng-Loo Lim).
5. Revising the manuscript together with all co-authors.

The attached manuscript and supplementary information are published in *Nano Letters* and were selected as the journal's *Front Cover Art*.

Parametric Amplification of Optical Pulses through Synthetic Motion in a Time-Varying Medium

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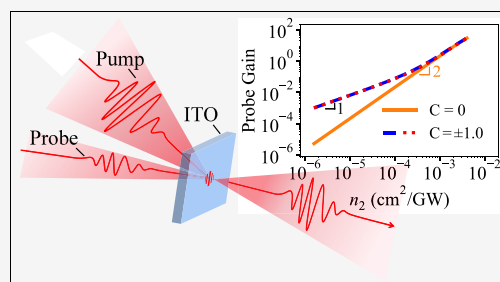
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ABSTRACT: Parametric amplification of optical waves conventionally requires phase matching and frequency offsets between interacting beams. Here, we demonstrate a fundamentally different amplification mechanism in epsilon-near-zero (ENZ) materials, where intense optical pumping creates a time-varying medium. We show, both theoretically and experimentally, that large spatiotemporal index modulations enable parametric amplification of frequency-degenerate pulses without requiring chirp or frequency offsets. The gain scales quadratically rather than linearly with the product of the pump intensity and the nonlinear refractive index coefficient n_2I , transitioning from conventional two-beam coupling to a regime dominated by time refraction. In a subwavelength-thick indium tin oxide film, we demonstrate significant probe amplification that overcomes the material's strong absorption. Our findings reveal that strong optical nonlinearities enable qualitatively new parametric processes, opening pathways for ultrashort-pulse amplification via dynamic metasurfaces and optical nanoswitches that exploit large gain modulation.

KEYWORDS: optical pulses, parametric amplification, ENZ materials, time-varying, optical pulses, two-beam coupling



Traveling-wave amplification is fundamental to both classical and quantum-mechanical devices. Two primary methods exist for amplifying optical pulses: employing a gain medium, such as an erbium-doped fiber, or harnessing nonlinear interactions, as in optical parametric amplifiers. However, both approaches typically require interaction lengths that are significantly longer than the wavelength scale to achieve meaningful gains. In gain media, the doping density is constrained by both chemical and physical limitations, whereas nonlinear methods are limited by the inherently weak nonlinearity of optical materials. The key challenge in this regard is finding mechanisms that enable substantial pulse amplification over the shortest possible propagation distance.

Parametric optical amplification exploits the second- or third-order nonlinearity of a material to transfer energy between optical signals. In third-order nonlinear media, two frequency-nondegenerate light beams of sufficient intensity can coherently exchange energy through a process called two-beam coupling (TBC).^{1–11} The most general case using continuous waves is shown in Figure 1a. According to the formalism of nonlinear optics, TBC can be explained as follows. The spatiotemporal interference of two beams—due to the frequency difference between them and the noninstantaneous response time of the material in which the beams are interfering—leads to the formation of a time-varying refractive index grating, which lags in the temporal phase behind the beat note of the driving fields, leading to a complex value of the

nonlinear contribution to the refractive index even when the nonlinear refractive index coefficient n_2 is purely real. The induced time-varying moving grating coherently scatters light energy from one beam to another, depending on its direction of motion. The direction and magnitude of the energy flow depend on several factors: the sign of the frequency difference, the intensities of the beams, the nonlinear refractive index coefficients, and the interaction length.

TBC is also shown for the case of pulsed beams (Figure 1b), provided that a moving interference pattern could be formed by instantaneous frequency differences between them due to the chirp.^{12–14} The instantaneous frequency difference and relative time delay between pulses determine the direction of energy transfer; in particular, a zero frequency difference results in zero energy transfer. A weak probe beam can be amplified by coherent energy transfer from an intense pump beam under specific conditions. For a positive value of the nonlinear coefficient n_2 , amplification occurs when the pump's instantaneous frequency exceeds that of the probe. TBC effects between both continuous and pulsed beams arise because the

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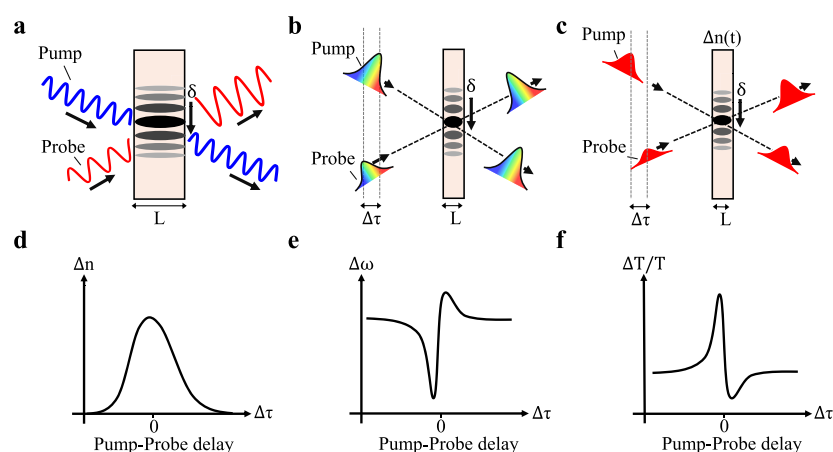


Figure 1. Overview of the two-beam coupling (TBC) in a nonlinear material with $n_2 > 0$. **a**, Continuous-wave TBC effect, where a moving grating with nonzero phase velocity, δ , is formed due to the frequency difference between two beams, leading to coherent energy transfer from the high-frequency beam (blue wave) to the low-frequency beam (green wave). **b**, Chirp pulse TBC effect, where an effective moving grating is formed when different frequency components of the pump and probe pulses interact within the medium, leading to energy transfer from pump to probe. **c**, The TBC effect in a time-varying medium is induced by an effective moving grating, which is formed by the temporal change in the refractive index ($\Delta n(t)$). This effect may not require chirping the laser pulses. **d**, The corresponding light-induced change in refractive index (Δn) as a function of pump–probe delay ($\Delta\tau$) and **e**, the change in frequency ($\Delta\omega$) due to time-refraction in a time-varying medium. **f**, Consequently, a transient, moving grating is formed, which leads to energy transfer.

total refractive index experienced by each wave is modified by the intensity of the other wave.¹⁰ The resulting gain scales linearly with the pump intensity, the intensity-dependent refractive index coefficient, and the interaction length. In a material with zero response time the two-beam coupling effect cannot occur, and thus a noninstantaneous response time is always required for TBC. However, even in a prototypical “instantaneous” Kerr material, such as fused silica, the nonlinear response time is nonzero,¹⁵ and thus TBC can occur.

The effect of TBC-induced gain can also be modeled using the formalisms of a time-varying medium. In essence, the spatiotemporal modulation of the index of a time-varying medium can amplify a weak beam. Recent experimental and theoretical reports have shown that a material whose refractive index is a strong function of time can be used to translate the frequency of an optical beam using the temporal analog of Fresnel refraction.^{16–20} An all-optical means of implementing a time-varying material is to use epsilon-near-zero materials. Such materials, when pumped by a short optical pulse, lead to a unity-order change in the refractive index.^{21–25}

In this work, we first examine TBC using numerical examples for various values of the nonlinear refractive index coefficient, n_2 . We find that for values of n_2 —and, by extension, the total change in index Δn —that lead to only perturbative index modification, the TBC between two pulses occurs only when the pulses are chirped. In contrast, nonperturbative Δn allows for TBC between a strong pump and a weak probe, even when the chirp vanishes. In this case, a large Δn leads to a large change in the time-dependent frequency shift of the probe beam; that is, the probe beam is chirped, and coherent energy transfer between the beams can occur. Consequently, the gain becomes a quadratic function of n_2 and pump intensity. This effect in a standard nonlinear optical material with perturbative nonlinearity is too weak to be measured experimentally.

Consider a typical frequency-degenerate pump–probe scheme as illustrated in Figure 1c. Figure 1d–f summarizes the process of two-beam coupling in a time-varying medium between pulses with zero initial chirp. When a strong pump pulse interacts with a medium, it induces a time-dependent

change in the medium’s refractive index ($\Delta n(t)$) that closely follows the temporal envelope of the pump pulse (Figure 1d). If a weak probe pulse interacts with the medium while the effects of the pump pulse are still present, the probe pulse will experience a change in refractive index and, as a result, will undergo frequency translation (Figure 1e). The frequency shift can be easily understood through the concept of time refraction.^{16,26–28} In contrast to refraction in space, the wavevectors, not the frequency, are conserved in the time-refraction process as the wave traverses a time-varying medium. A beam of light redshifts (blueshifts) if it experiences an increase (decrease) in the refractive index while traveling through the medium. Materials excited by an optical pulse with energy below the damage or phase-transition thresholds eventually return to their ground states. Thus, a weak probe pulse can experience either an increase or a decrease in refractive index, depending on the pump–probe delay and the material’s response times. The index change and the resulting changes in pulse frequency suggest that even degenerate, initially unchirped pulses could produce a moving interference grating between them and, consequently, coherently transfer energy between the pulses, resulting in a TBC-driven change in the probe transmission (Figure 1f).

The set of coupled equations that describes the TBC process in a medium is presented in the Supporting Information. We adopted the formalisms presented by Smolorz, Wise, and Borrelli.^{7,8} We present our primary numerical findings in Figure 2. First, we test the validity of our model and identify the regimes of coherent energy transfer from a purely phase-grating formation. Figure 2a shows the TBC calculations in a conventional material, a 120 μm , thick fused silica with an n_2 of $3.2 \times 10^{-7} \text{ cm}^2/\text{GW}$, for identical pump and probe pulses (100 fs, at 1300 nm, 100 GW/cm²) as a function of the time delay between the pulses, $\Delta\tau$. We trace out the normalized change in the transmittance of the probe, $\Delta T/T = (T_{\text{Nonlinear}} - T_{\text{Linear}})/T_{\text{Linear}}$, for various input chirp values.⁸ Normalizing with respect to linear transmission enables us to isolate the effects that lead to nonlinear changes in transmission by incorporating linear Fresnel coefficients, like reflection and absorption. We

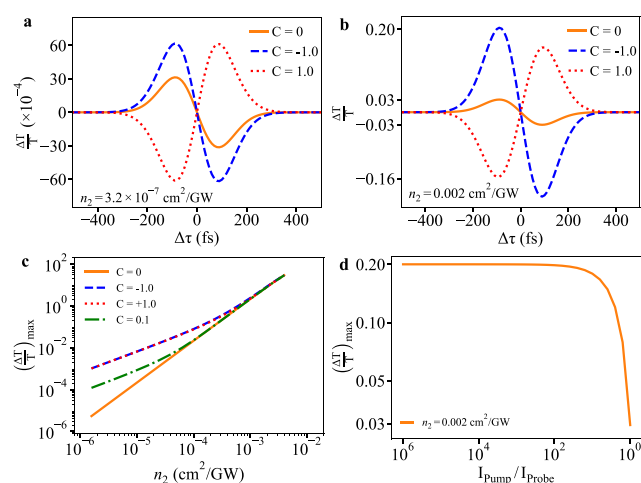


Figure 2. Numerical results showing the effect of chirp in TBC. **a**, Normalized changes in transmittance ($\Delta T/T$) as a function of delay time ($\Delta\tau$) in fused silica ($n_2 = 3.2 \times 10^{-7} \text{ cm}^2/\text{GW}$) with various chirp values— $C = -1$ (blue line), 0 (orange line), and 1 (green line)—for a propagation distance of $120 \mu\text{m}$. The curve for $\frac{\Delta T}{T}$ for the $C = 0$ case is magnified 100 times. **b**, In contrast, the magnitude of TBC between pulses with zero chirp in a material with stronger nonlinearity ($n_2 = 2 \times 10^{-3} \text{ cm}^2/\text{GW}$) is significantly larger. **c**, Maximum $\Delta T/T$ as a function of nonlinear refractive index coefficient n_2 for various values of chirp. For large nonlinearity, TBC between a pair of unchirped pulses is as strong as for pulses with strong chirp and is a quadratic function of the refractive index coefficient. **d**, The strength of the TBC effect also depends on the relative intensity of the pump and the probe beam. The probe needs to be at least 2 orders of magnitude weaker than the pump to avoid saturation effects.

observe that the magnitude of energy transfer for a pair of Fourier-transform-limited Gaussian pulses ($C = 0$) is 200 times lower than that of pulses with a small input chirp ($C = \pm 1.0$). This confirms what is already known about pulse TBC: for small n_2 values, a positive or negative chirp induces a moving grating, provided the material experiences a frequency difference. Figure 2b shows that for a much larger value of n_2 (the propagation length is decreased to 620 nm), TBC between a pair of pulses with $C = 0$ becomes more significant. This shows why it has not been possible to observe the TBC effect in standard nonlinear optical materials—where n_2 values are significantly smaller—without using chirped pulses. The normalized probe transmission in this case is 1000 times higher than in the fused silica case.

Next, we investigate the scaling of TBC with the magnitude of n_2 . We show our results in Figure 2c. We perform a series of calculations of the TBC in a $4 \mu\text{m}$ thick material as a function of the n_2 values. Here, n_2 refers to $n_{2,\text{cross}}$, which is the effective nonlinear index of refraction experienced by a pulse due to the intensity of another pulse. As shown in Figure 2c, for $C \neq 0$, when n_2 is small, the TBC effect is linear to n_2 values; thus our formalism reproduces the well-known result of TBC. However, for a given chirp value, the magnitude of TBC becomes quadratic to n_2 for larger values of n_2 , irrespective of the magnitude and sign of the chirp. The range of n_2 values in which the transition from linear to quadratic scaling occurs depends on how chirped the beams are. Essentially, the transition occurs under the operating conditions where, due to the large values of n_2 , and by extension large $\Delta n = n_2 I$, the nonlinearity-induced frequency translation (that is, a time-dependent ramp in frequency) becomes large enough to be

comparable with the existing chirp of the pulses. The sign of n_2 also plays a crucial role. As shown in Figure 2b, a positive value of n_2 contributes constructively to the TBC signal in the case of a negative chirp. That is because a positive value of n_2 up-chirps the pulses. Finally, in Figure 2d, we demonstrate that the magnitude of small-signal amplification in a strongly nonlinear medium decreases with increasing probe intensity while keeping the pump intensity constant (i.e., with increasing $I_{\text{pump}}/I_{\text{probe}}$). For example, in the case of unchirped beams of equal intensities, the maximum value of $\Delta T/T = 0.03$ (the orange line of Figure 2b) increases by an order of magnitude when the intensity of the probe is sufficiently decreased with respect to the pump (Figure 2d). This qualitative behavior is also consistent with broadband amplification schemes experimentally shown by Vampa et al.²⁹ and the concept of amplification due to the modulation instability first described by Bespalov and Talanov in the case of spatial instability.^{30,31}

Next, we experimentally investigate TBC for large values of $n_2 I$. To experimentally demonstrate TBC in the regime of large n_2 (and large Δn), we use a 620 nm -thick indium tin oxide (ITO) film excited by $\sim 90 \text{ fs}$ pump and probe pulses in the frequency range where the linear permittivity of ITO is near zero, i.e., in the epsilon-near-zero (ENZ) regime (see Supporting Information). In this operation regime, ITO exhibits 5 orders of magnitude larger nonlinearity than that of fused silica.^{32,33} The total change in index $\Delta n \approx 0.75$ occurs within a subpicosecond time scale.³⁴ Due to the large modulation of the refractive index, broadband frequency shifts of up to 15 THz are also reported,¹⁶ making ITO an ideal material for studying TBC in the limit of large n_2 . The Drude model accurately describes the linear optical properties of ITO in the spectral region of interest in this work. The zero-permittivity wavelength of the film is around 1240 nm . We conducted a series of degenerate pump–probe experiments with an angular separation of 7° between the beams to characterize the magnitude of the two-beam coupling process. Both pulses are chirped with $C \sim 1.3$, as confirmed by frequency-resolved optical gating (FROG) measurements (see Supporting Information). The free-electron-driven nonlinear optical responses present in ITO and similar ENZ materials are similar to those of novel metals and different than that of the traditional bound electron nonlinearity of a dielectric. Thus, it is appropriate to use $n_{2,\text{eff}}$ to denote the “Kerr-type” nonlinearity of these ENZ materials. However, for the sake of brevity, we choose to use n_2 throughout this paper. Multiple investigations have used thermodynamic models to describe the nonlinear response of transparent conducting oxides in the ENZ spectral region.^{35–40} However, here, we ignore the microscopic origin of the nonlinearity. In doing so, our goal is to draw attention to the universal effects arising from the large values of intensity-dependent refractive index change, for which ITO is a convenient example material. Furthermore, the model adopted here to describe light–matter interactions ignores the underlying microscopic origins of the index change, as the change itself, independent of its origin, determines the results shown here. As shown in our numerical analysis above, for large values of n_2 , regardless of the chirp value, the magnitude of energy transfer is quadratic in n_2 and intensity I . Although pulses free from the chirp of any order would have been an ideal source for the experiment, we avoided manipulating the chirp of the beams to avoid the increased complexity of the experiment. Furthermore, this work aims to experimentally establish the quadratic scaling of the induced

gain with intensity and n_2 , rather than the well-known linear scaling observed in TBC. Our results indicate that, even though a large chirp is present in our beams—produced by an optical parametric amplifier pumped by a 90 fs laser source—quadratic scaling still holds.

We first measure the $\Delta T/T$ of the weak probe beam (0.8 GW/cm²), as a function of pump–probe delay ($\Delta\tau$) for varying pump intensities between 4 GW/cm² and 500 GW/cm² as shown in Figure 3a. Both pump and probe beams are

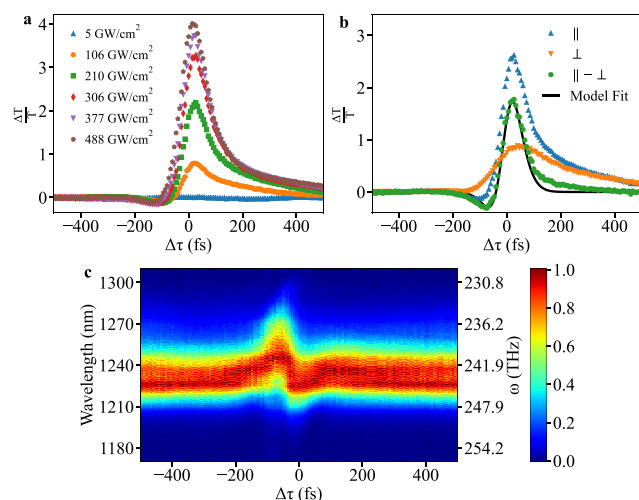


Figure 3. TBC effect in an ENZ material. **a**, The measured normalized change in transmission, $\frac{\Delta T}{T}$, for the pump–probe polarization parallel to each other, shown for various pump intensities ranging from 4 to 500 GW/cm². **b**, The measured $\frac{\Delta T}{T}$ for the probe polarization perpendicular to the pump (orange dots), parallel to the pump (blue dots), and their difference (green dots), at a pump intensity of 240 GW/cm². The black line shows the model fit obtained using the coupled-mode equations described in the Supporting Information. **c**, The measured probe spectrum as a function of pump–probe delay ($\Delta\tau$) at a pump intensity of 240 GW/cm².

centered at 1240 nm, with the probe beam incident normally onto the sample. In the presence of the pump beam, the probe beam transmittance changes significantly, exhibiting increased modulation at higher pump intensities. Because the pulses have a positive chirp, we expect to see a drop in probe transmission for small, negative $\Delta\tau$ values, followed by an increase for positive $\Delta\tau$ values, as shown in Figure 2b, with the first change being smaller than the second due to a significant difference in pump and probe intensity. The dips in the probe beams for negative pump–probe delay are the signature TBC behavior and have been reported previously for other materials.^{8,10,41} The TBC model presented in the Supporting Information fully captures this behavior.

However, we must consider that the measured probe transmission is subject to multiple nonlinear influences: 1) coherent energy transfer from the pump to the probe; 2) a decrease in absorption;³⁴ and 3) an increase in input power due to decreased Fresnel reflection.³⁴ In general, all three effects can occur simultaneously if the pump and probe are copolarized. However, if the pump and the probe beams are orthogonally polarized, only the latter two effects are present.¹¹ We characterize the TBC in ITO using the following procedure. First, we measure the $\Delta T/T$ of a weak probe

beam as a function of the delay between the p-polarized pump and probe for two cases: probe polarization parallel (p-polarized) or perpendicular (s-polarized) to the p-polarized pump. The difference between the two measurements is the TBC signal, which represents coherent energy transfer resulting from a change in the real part of the refractive index. Figure 3b shows how the TBC influence on $\Delta T/T$ is isolated from the difference of cross- and copolarized transmission measurements for a representative pump intensity of 240 GW/cm². We define the maximum of this differential

signal $\left(\left(\frac{\Delta T}{T}\right)_{\max}\right)$ as the gain of the probe pulse, i.e., the amount by which TBC amplifies the probe pulse. The peak gain shown in Figure 3b is 1.78. Fitting our TBC theoretical expressions shown in the Supporting Information to these results suggests that the value of n_2 is 0.002 cm²/GW, which is consistent with expectations for ITO in these conditions.³⁴ The asymmetry in Figure 3b stems from the asymmetry of the pump-induced change in the refractive index of ITO. We observe a rise time of 220 fs and a fall time of 363 fs, which is consistent with previous reports on ITO.^{23,34} We also simultaneously record the probe spectrum as a function of the pump–probe delay (Figure 3c). We observe that the probe pulse redshifts at the rising edge of the pump and then blueshifts as the pump–probe delay increases. These results are consistent with previous reports^{16,18,23,24,26,42,43} and demonstrate that the material under study behaves as a medium varying in time.

For large nonlinearity, the probe pulse amplification also depends quadratically on the pump intensity. To demonstrate this effect, we performed two sets of pump-intensity-dependent measurements at two different angles of incidence, each at 1240 nm. At ENZ wavelengths, the n_2 values of ITO depend on the angle of incidence.³⁴ Thus, by varying the angle of incidence on the ITO film, we naturally obtain a medium whose nonlinear coefficient can be varied significantly. Here, n_2 denotes the experimentally measured effective nonlinear coefficient and necessarily includes all mechanisms of angle-dependent enhanced light–matter interactions arising from structural and material effects. Thus, the $n_2(\theta)$ of a subwavelength-thick ENZ film can be different from that of a bulk n_2 . We choose 0° and 40° angles of incidence for the probe beam. We present the intensity-dependent gain measurements in Figure 4a. We find that, in general, the gain varies nearly quadratically with the pump beam intensity. We experimentally find that for a 0° angle of incidence, the gain scales as $I^{1.81}$, whereas for 40°, the gain is proportional to $I^{1.95}$. The difference in these dependencies can be explained by the n_2 value at a 40° angle of incidence being almost an order of magnitude larger than that at 0°. We also find that at sufficiently high intensities, the gain saturates and deviates from quadratic scaling. This could be explained by the transient redshift of the system's effective plasma frequency due to optical excitation, leading to a decrease in the ENZ-led enhancement in nonlinear responses. Furthermore, data for 40° angles of incidence show that saturation is reached at a significantly lower intensity than the saturation threshold at 0°. For the thicknesses we used, we cannot necessarily attribute the low-power onset of saturation at a larger angle of incidence solely to the excitation of the Berreman mode. The inefficient excitation of this mode and the associated field enhancement still play a noninsignificant role in lowering the threshold. In an ENZ medium, angle-dependent enhancement of n_2 values has

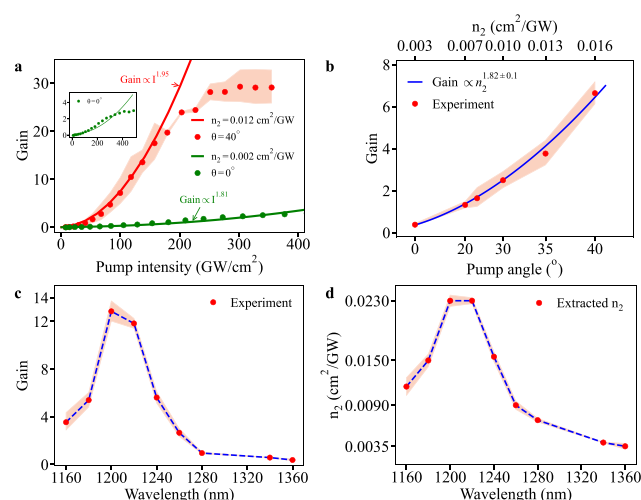


Figure 4. Experimental observation of amplification in a time-varying medium. **a**, The measured gain as a function of pump intensity (GW/cm²) for incidence angles of 0° (green dots) and 40° (red dots). Solid lines are generated using coupled-mode equations as presented in the Supporting Information. For larger values of n_2 , the gain becomes nearly quadratic in the pump intensity I . **b**, The measured gain as a function of angles of incidence in ITO and by extension various n_2 values of ITO. We extracted n_2 values using the couple-mode equations for various angles of incidence of the probe. **c**, The measured gain as a function of input wavelength. The maximum gain is observed at 1200 nm, which falls within the ENZ wavelength range of our sample. **d**, Extracted n_2 as a function of wavelengths in the epsilon-near-zero region of the ITO. The observed peak at zero-crossing wavelength of ITO is consistent with previous reports.³⁴

been previously reported.³⁴ Although the values of n_2 vary as a function of incidence angles, the maximum underlying change of the index $\Delta n = n_2 I$ remains constant, regardless of the angle of incidence. Thus, a larger n_2 value necessarily leads to the saturation of the gain at a lower pump intensity. By varying the pump (and probe) angle for a constant pump intensity below saturation for all angles (66 GW/cm²) and recording the TBC probe gain, we confirmed the near-quadratic dependence on n_2 in Figure 4b, as predicted in Figure 2c. This quadratic behavior represents the main signature of TBC via time-refraction. It has never been observed in conventional materials such as fused silica, simply because their weak optical nonlinearity⁸ confines them to the chirp-dominated regime. Short of saturation or higher-order effects, increasing n_2 or I_{pump} will cause the TBC-based gain of a probe to approach 2 asymptotically.

Next, we investigate the probe-pulse gain as a function of wavelength, while keeping all other operating conditions constant. Figure 4c shows how the gain of the weak probe pulse varies as a function of wavelength. For this set of measurements, we choose the pump's angle of incidence to be 47° and the probe's angle of incidence to be 40°. We also set the peak intensity of the pump pulses at 66 GW/cm². We choose the intensity value to be sufficiently far from the gain-saturation regime for all wavelengths of interest. We find that the wavelength-dependent gain curve peaks near ENZ wavelengths. We extract the n_2 values from these measurements and present the results in Figure 4d. Even in this case, the gain remains approximately quadratic, $n_2^{1.83}$ (see Supporting Information), relative to the wavelength-dependent values of n_2 .

A typical metal suffers from loss at optical frequencies.⁴⁴ Consequently, metal-based metamaterials also exhibit non-negligible loss. Significant efforts have been made to pair lossy metals with a gain material to compensate for loss and achieve lasing.^{44–47} Despite metals being highly nonlinear, achievable parametric gains using surface plasmon polaritons in noble metals are limited.^{48,49} In ENZ materials, the subwavelength thickness and the near-zero refractive index enable phase-mismatch-free nonlinear interactions,⁵⁰ and thus multiple nonlinear processes occur simultaneously, e.g., four-wave mixing (FWM)^{51,52} and harmonic generation.^{53,54} However, in our analysis of TBC, we have ignored all other energy transfer processes. The largest of all these is the FWM, and the maximum efficiency is less than 12%.⁵¹ The maximum energy transfer due to FWM occurs at zero delay between the pump and the probe, whereas the maximum energy transfer from the pump to the probe due to the TBC effect occurs at a delay time $\Delta\tau \approx 25$ fs. Thus, the uncertainty arising from ignoring FWM is no more than a few percentage points in determining the n_2 and the gain coefficient values. Our results point to the future possibilities of combining ENZ materials with plasmonic metals⁵⁵ for significant parametric amplification of plasmon polaritons. Furthermore, a sufficiently large parametric gain could enable the observation of exotic linear ENZ behavior, such as supercoupling, at optical frequencies.⁵⁶ Two-beam coupling underlies numerous phenomena, from stimulated Raman scattering to the nonlinear response of a two-level atom. Our findings suggest that these “well-understood” processes may behave fundamentally differently and require revisiting in emerging materials with extreme properties, including highly nonlinear metasurfaces, quantum materials, and strongly driven twisted-2D materials. Our work provides the theoretical and experimental framework for predicting and exploiting qualitatively new phenomena that emerge when material responses become nonperturbative.

In conclusion, we have experimentally observed, for the first time, that coherent energy transfer between a pair of frequency-degenerate pulses exhibits a quadratic dependence on $n_2 I$ at large $n_2 I$. These features of TBC have not been experimentally reported so far due to the weak values of n_2 in most conventional nonlinear optical materials. We have exploited the large nonlinearity to demonstrate the amplification of a ~ 90 fs pulse while it propagates through a subwavelength-thick film. We note that the effect can be further engineered to induce a significantly larger gain using an ENZ- or other semiconductor-based metasurfaces or stacks of 2D materials.⁵⁷ Thus, our results open up the possibility of designing amplifying metasurfaces for classical and quantum optical applications and amplification of ultrashort pulses using nanomaterials.^{58–61}

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.5c05821>.

Detailed derivations of the nonlinear coupled-mode equations used in modeling, the experimental extraction of parametric gain, and the impact of linear losses in ITO on gain; the pump–probe experimental setup, frequency-resolved optical gating (FROG) measurements for ultrafast pulse characterization, and linear optical characterization of the ITO thin films (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information for: Parametric amplification of optical pulses through synthetic motion in a time-varying medium

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SUPPLEMENTAL NOTE 1: NONLINEAR COUPLED-MODE EQUATIONS

To simulate the two-beam coupling (TBC) effect, we adopted the mathematical model reported by Smolorz and Wise [1] and provided an overview of the model in this section. The total field of the two beams must satisfy the nonlinear wave equation

$$\left(\frac{\partial^2}{\partial z^2} - \frac{n_0^2}{c^2} \frac{\partial^2}{\partial t^2} \right) E(z, t) = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} P_{\text{NL}}(z, t),$$

where $P_{\text{NL}}(z, t)$ is the nonlinear polarization term which depends on the response function, $R_{\text{NL},ijkl}(t - t')$ of the material

$$P_{\text{NL},j}(\mathbf{r}, t) = \sum_{i,k,l} E_i(\mathbf{r}, t) \int_{-\infty}^t dt' R_{\text{NL},ijkl}(t - t') E_k(\mathbf{r}, t') E_l(\mathbf{r}, t').$$

In our case, we are interested in the coherent energy transfer that arises from the real part of the nonlinear refractive index. The response function is

$$R_{\text{NL}}(t - t') = \frac{R_{\text{NL}}^0}{T_{\text{R}}} \exp \left[-\frac{(t - t')}{T_{\text{R}}} \right],$$

where R_{NL}^0 is the nonlinear refractive index and T_{R} is the response time of the material. When the pump and probe are delayed with respect to each other $\Delta\tau$ (similar to Fig.1a), the total electric field is

$$E(z, t) = A_1(t - \Delta\tau) \exp\{-i[\omega_1(t - \Delta\tau) - k_1 z]\} + A_1^*(t - \Delta\tau) \exp\{i[\omega_1(t - \Delta\tau) - k_1 z]\} \\ + A_2(t) \exp[-i(\omega_2 t - k_2 z)] + A_2^*(t) \exp[i(\omega_2 t - k_2 z)].$$

We define the field amplitude of a linearly chirped Gaussian pulse with chirp factor C as

$$A(t) = A \exp \left[-\frac{t^2(1 + iC)}{2t_0^2} \right],$$

which leads to a time-dependent frequency shift of

$$\delta\omega = \frac{tC}{t_0^2}.$$

Upon substituting the electric field corresponding to two Gaussian pulses and also the material response function into the nonlinear wave equation, and using the slowly varying amplitude approximation, we get the following nonlinear coupled-mode equations

$$\frac{dA_1}{dz} = i2\pi k_1 [A_1(t - \Delta\tau)H_1 + A_1^*(t - \Delta\tau)H_2 + A_2(t)H_4 + A_2(t)^*H_3], \quad (1)$$

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$$\frac{dA_2}{dz} = i2\pi k_2 [A_2(t)H_1 + A_2^*(t)H_5 + A_1(t - \Delta\tau)H_4^* + A_1(t - \Delta\tau)^*H_3], \quad (2)$$

where

$$H_1 = \int_{-\infty}^t R_{\text{NL}}(t - t') [2|A_1(t' - \Delta\tau)|^2 + 2|A_2(t')|^2] dt', \quad (3)$$

$$H_2 = \exp(2i\omega_1 t) \int_{-\infty}^t R_{\text{NL}}(t - t') A_1(t' - \Delta\tau)^2 \exp(-2i\omega_1 t') dt', \quad (4)$$

$$H_3 = \exp(i\Omega t) \int_{-\infty}^t R_{\text{NL}}(t - t') 2A_1(t' - \Delta\tau)A_2(t') \exp(-i\Omega t') dt', \quad (5)$$

$$H_4 = \exp(i\Delta\omega t) \int_{-\infty}^t R_{\text{NL}}(t - t') 2A_1(t' - \Delta\tau)A_2^*(t') \exp(-i\Delta\omega t') dt', \quad (6)$$

$$H_5 = \exp(2i\omega_2 t) \int_{-\infty}^t R_{\text{NL}}(t - t') A_2(t')^2 \exp(-2i\omega_2 t') dt', \quad (7)$$

where $\Delta\omega = \omega_1 - \omega_2$ and $\Delta\Omega = \omega_1 + \omega_2$. For Fourier-transformed Gaussian pulses with chirp we need to include the time-dependent frequency shift due to chirp, $\Delta\omega = (\omega_1 + \frac{(t - \Delta\tau)C}{t_0^2}) - (\omega_2 + \frac{tC}{t_0^2})$. H_1 and H_4 terms correspond to the purely refractive two-beam coupling (TBC) contribution and chirp-based TBC, respectively. H_1 term includes the contribution of self and cross-phased modulation experienced by the probe beam. H_2 , H_3 and H_5 terms oscillate at $2\omega_1$, $\omega_1 + \omega_2$ and $2\omega_2$ frequencies respectively - higher frequencies than the input beams. After making the rotating-wave approximation, i.e., keeping only the terms that are nearly stationary with respect to A_1 , we obtain the following coupled-mode equations, which retain H_1 and H_4 terms for the TBC simulations.

$$\frac{dA_1}{dz} = i2\pi k_1 [A_1(t - \Delta\tau)H_1 + A_2(t)H_4], \quad (8)$$

$$\frac{dA_2}{dz} = i2\pi k_2 [A_2(t)H_1 + A_1(t - \Delta\tau)H_4^*]. \quad (9)$$

We solve coupled-mode equations, Eq. 8 and Eq. 9 numerically using Mathematica to obtain the probe envelope $A_1(t, z)$ at the input ($z = 0$) and output ($z = L$) of the sample. The normalized change in probe transmission is then calculated as the relative change in time-integrated probe intensity:

$$\frac{\Delta T}{T}(\Delta\tau, R_{\text{NL}}) = \frac{\int_{-\infty}^{\infty} |A_1(z = L, t)|^2 dt - \int_{-\infty}^{\infty} |A_1(z = 0, t)|^2 dt}{\int_{-\infty}^{\infty} |A_1(z = 0, t)|^2 dt}. \quad (10)$$

$A_1(t, z)$ depends on the amplitude of both the pulses - the pump and probe intensities, chirp, nonlinear refractive index of the material, response time of the material, and the interaction length. By varying the relative contributions of the nonlinear refractive index, pump intensity, and interaction length to the nonlinear change of probe transmission, we can model the coherent energy transfer from pump to probe.

SUPPLEMENTAL NOTE 2: EXPERIMENTAL SETUP

We used a wavelength-tunable optical parametric amplifier, pumped by an amplified Ti:Sapphire laser (TOPAS Prime, Spectra-Physics), to generate ~ 90 fs laser pulses. A pellicle beam splitter (BP245B3, Thorlabs) split the output laser beam of OPA into two separate beams that propagate to the probe and pump lines. We then independently

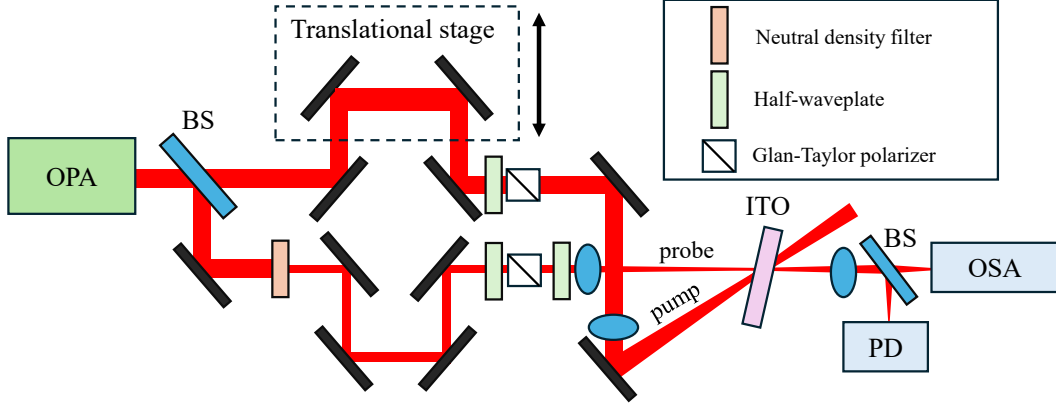


FIG. S1. **The schematic of the experimental setup.** BS: pellicle beamsplitter. OPA: optical parametric amplifier. OSA: optical spectrum analyzer. PD: photodetector

tuned the intensities of both beams using a pair of half-wave plates mounted on rotational stages and Glan-Taylor polarizers. Both pulses are set to be p-polarized. A 100-mm lens focused the probe pulse on the sample, and the corresponding beam size (full-width-half-maximum (FWHM)) is ~ 52 microns. A 150-mm lens focuses the pump pulse, and the FWHM beam size is ~ 83 microns. The pump and probe pulses are separated by 7° throughout all the experiments. A motorized translation stage (DDSM100, Thorlabs) controlled the delay time between the probe and pump pulses. InGaAs photodetectors (918D-IG-OD3R, Newport) measure the input and transmitted powers of the pump and probe. We also measure the first-order diffraction to ensure both beam's spatio-temporal overlap. For input beam power measurement, a calibrated glass slide reflects a small portion of the beam, and the photodetectors collect it. Figure S1 shows the schematic of the experimental setup. Input powers are measured using calibrated glass slides that reflect a small portion of the beam to the photodetectors.

SUPPLEMENTAL NOTE 3: LINEAR OPTICAL PERMITTIVITY OF ITO

The real and imaginary parts of the optical permittivity of the ITO film used in this work are shown in Figure S2. The ENZ wavelength of this sample is 1240 nm.

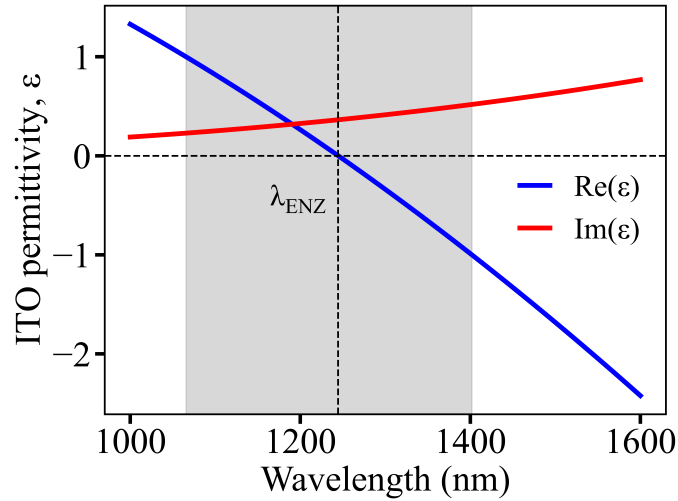


FIG. S2. **Optical permittivity of ITO** The real (blue) and the imaginary (red) parts of ITO permittivity as a function of laser wavelength. The ENZ wavelength of this sample (λ_{ENZ}) is 1240 nm.

SUPPLEMENTAL NOTE 4: FREQUENCY-RESOLVED OPTICAL GATING (FROG) MEASUREMENTS

We performed a series of phase-gating frequency-resolved optical gating (PG-FROG) measurements to characterize the laser pulse[2, 3]. We used a 2-mm-thick glass slide to implement PG-FROG. Figure S2a shows the spectrum of the laser pulse with a bandwidth of 47 nm, and the central wavelength of the laser pulse is 1240 nm. Next, we applied phase-retrieval algorithms to obtain the pulse's phase and amplitude, finding that the pulse duration measured by PG-FROG is ~ 90 fs. Figure S3b shows the phase-retrieval results. We obtained the corresponding laser pulse's chirp (C) by using the following equation:

$$\Delta\omega_{BW} = (1 + C^2)^{1/2} / T_0 \quad (11)$$

where $\Delta\omega_{BW}$ is the frequency bandwidth of the laser pulse, and t_0 is the pulse duration. The obtained C is 1.58.

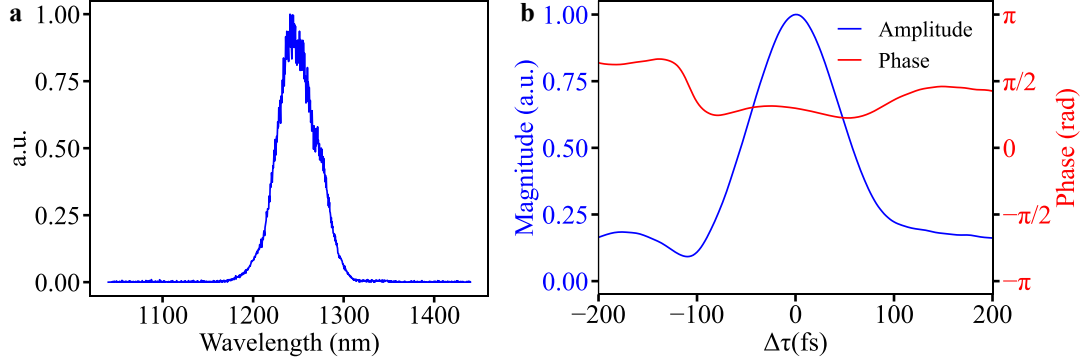


FIG. S3. *

PG-FROG results. (a) The laser pulse spectrum has a bandwidth of 47 nm. (b) The obtained amplitude and phase of the laser pulse at 1240 nm using phase-retrieval algorithms and PG-FROG.

SUPPLEMENTAL NOTE 5: EXPERIMENTAL EXTRACTION OF GAIN

There are three reasons for changes in the probe beam's nonlinear transmittance. 1. Coherent energy transfer from the pump to the probe. 2. A nonlinear decrease in the imaginary part of the refractive index due to the intensity of the pump beam. 3. A drop in Fresnel reflectance due to an increase in the linear part of the refractive index. The latter two effects are parasitic and need to be accounted for to be able to isolate these incoherent effects from the true coherent amplification. We undertook the following procedures to quantify and isolate the coherent contribution from the incoherent contributions. We first fix the pump polarization to p and measure $\frac{\Delta T}{T}$ for p-polarized ($\parallel$) and s-polarized ($\perp$) probe. Upon subtracting $(\frac{\Delta T}{T})_{\parallel} - (\frac{\Delta T}{T})_{\perp}$, we get the coherent energy transfer due to the real part of the refractive index. We employ an additional half-waveplate on the probe arm, after the Glan-Taylor polarizer, to rotate the probe beam's polarization. As we increase the pump angle, we must also account for the pump's angle-dependent Fresnel coefficients. In addition to $(\frac{\Delta T}{T})_{\parallel} - (\frac{\Delta T}{T})_{\perp}$ when pump is p-polarized and probe is p and s polarized, we also measure $(\frac{\Delta T}{T})_{\parallel} - (\frac{\Delta T}{T})_{\perp}$ when the probe is p-polarized and pump polarization is p and s. We take the geometric mean of both $(\frac{\Delta T}{T})_{\parallel} - (\frac{\Delta T}{T})_{\perp}$ and report it as Gain in the Fig. 4 of the main text.

SUPPLEMENTAL NOTE 6: THE EFFECT OF LOSS

In the previous section, we addressed how we mitigate the strong change in output power due to the intensity-dependent drop in the absorption. Although we have followed the standard definition of TBC gain in the main text, here we provide a more nuanced analysis of the effect of linear absorption on the z-dependent power. Linear loss in the pump affects the effective nonlinear length. In contrast, the probe experiences both amplification and absorption. Our experimental result shows that, in the presence of the pump, the probe experiences amplification regardless of the angle of incidence. We use a simple model to understand how the power carried by the probe wave varies with

propagation distance along z . At 40° incidence, the linear reflectance, $R_{\theta,linear}$ and linear transmittance, $T_{\theta,linear}$ for 620 nm of ITO are 0.28 and 0.0041. Using Beer-Lambert law, we can calculate the absorption coefficient as

$$\alpha = -\frac{1}{L_\theta} \ln\left(\frac{T_{linear}(\theta)}{1 - R_\theta}\right), \quad (12)$$

where $L_\theta = L/\cos(\theta)$ is the effective optical thickness of the ITO layer at angle θ . In our case, $\alpha = 0.0064 \text{ nm}^{-1}$. The normalized probe output power as a function of propagation distance is calculated using

$$P_{out,linear}(\theta) = (1 - R_{\theta,linear}) \exp(-\alpha L_\theta), \quad (13)$$

and shown in Figure S5a. The probe Gain(θ, I_{pump}) is defined in note 5 as

$$\text{Gain}(\theta, I_{\text{pump}}) = \frac{\Delta T}{T} = \frac{T_{\text{nonlinear}} - T_{\text{linear}}}{T_{\text{linear}}}, \quad (14)$$

Assuming an exponential response, the nonlinear to linear transmission ratio becomes as

$$\frac{T_{\text{nonlinear}}(\theta)}{T_{\text{linear}}(\theta)} = 1 + \text{Gain}(\theta, I_{\text{pump}}) = \exp\left(g(\theta, I_{\text{pump}}) L_{\text{eff},\theta}\right), \quad (15)$$

where $L_{\text{eff},\theta} = \frac{1 - \exp(-\alpha L_\theta)}{\alpha}$ is the effective nonlinear interaction region. From the measured Gain after 620 nm of thickness, the gain coefficient, $g(\theta, I_{\text{pump}})$, is extracted using

$$g(\theta, I_{\text{pump}}) = \frac{\ln[1 + \text{Gain}(\theta, I_{\text{pump}})]}{L_{\text{eff},\theta}}. \quad (16)$$

Using the computed gain coefficients $g(\theta, I_{\text{pump}})$ for 300 GW/cm² of pump intensity and $P_{out,linear}(\theta, \lambda)$, we can compute the $P_{out,nonlinear}(\theta, \lambda)$ as

$$P_{out,nonlinear}(\theta) = (1 - R_{\theta,linear}) \exp(-\alpha L_\theta) \exp\left(g(\theta, I_{\text{pump}}) L_{\text{eff},\theta}\right). \quad (17)$$

Figure S4a shows the normalized probe output power for the case with Gain with respect to the length of ITO for a 40° angle of incidence for a pump intensity of 300 GW/cm². Figure S4b shows the same for the case of Fresnel-adjusted reflections, and we can see in Figure S4a that the probe is amplified by a factor of ~ 3 over about ~ 200 nm. In Figure S5, we show nonlinear transmission of probe at 40 degrees angle of incidence as a function of both pump intensity and propagation length in ITO, which indicates a region of amplification for pump intensities greater than 100 GW/cm² and propagation lengths less than 250 nm.

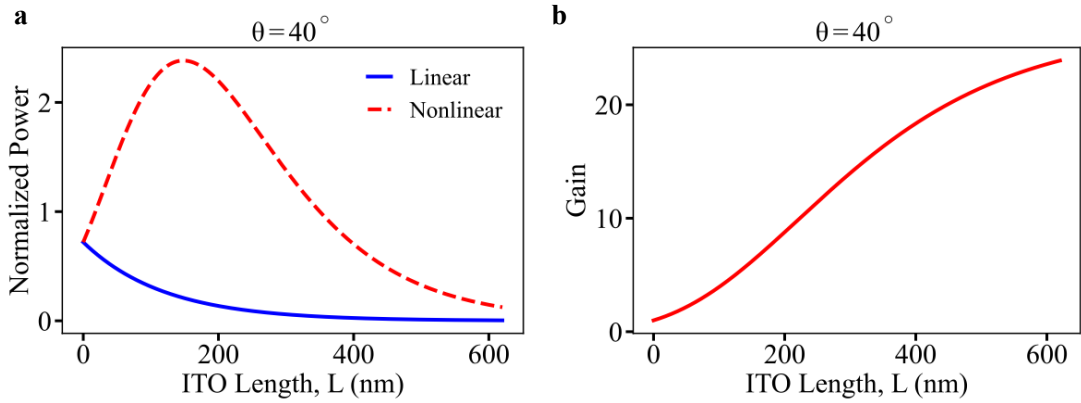


FIG. S4. Linear and nonlinear change in power of probe at 1240 nm with respect to ITO length for (a) 40° angle of incidence and (b) shows the amplification factor of the probe as a function of longitudinal distance.

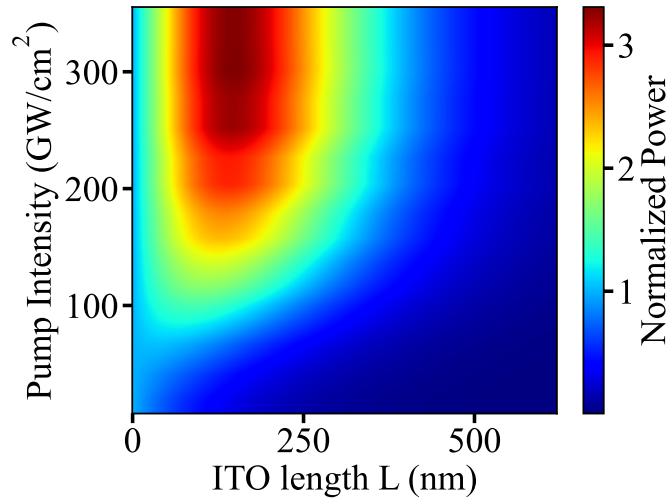


FIG. S5. Fresnel-reflection-adjusted nonlinear transmittance of a probe as a function of the intensity of the pump beam and the propagation length at 1240 nm. The angle of incidence, $\theta = 40^\circ$.

SUPPLEMENTAL NOTE 7: QUADRATIC DEPENDENCE OF GAIN

In Fig. 4c and Fig. 4d of the main text, we show the Gain with respect to different wavelengths and the corresponding dispersion of n_2 with respect to the wavelength. Figure S6 shows the quadratic dependence of Gain on n_2 .

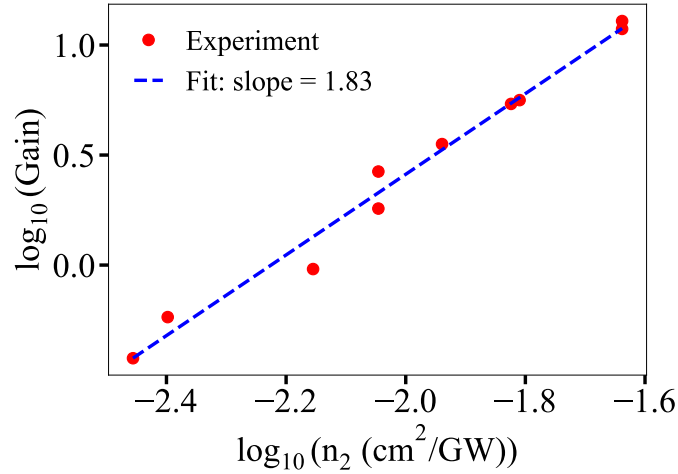


FIG. S6. Log-log plot to show the quadratic dependence of Gain on n_2 (n_2 for different wavelengths)

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Chapter 3

Ultrafast dynamics of the excitation of a Brewster mode in an epsilon-near-zero-based nanocavity

Contribution Statement

Dr. Zahirul Alam and Dr. Rasoul Alaei conceived the idea of fabricating a Gires-Tournois nanocavity with one reflector being an ITO thin film, motivated by the large refractive-index changes observed in ITO thin films and the large resonance shifts previously observed in plasmonic nanoantennas on ITO substrates experiencing this index change. The goal was to investigate whether cavity modes would experience a similarly large resonance shift when the refractive index of ITO is optically modified. A series of such devices was fabricated by Dr. Shivashankar Vangala and Dr. Joshua R. Hendrickson and sent to us for characterization. The initial plan was

to observe optical switching of the cavity modes by optically changing the refractive index of ITO.

At that time, I was working on optical switching using ITO/Au nanostructures. Using the same nonlinear pump-signal experimental setup, Theng-Loo Lim and I began characterizing the fabricated samples. We conducted all the linear and nonlinear experiments under the guidance of Dr. Zahirul Alam. This work examines how the signal pulse's reflection from the sample changes as the pump pulse alters the cavity modes. For sufficiently high pump powers, the cavity mode (fields predominantly in the cavity) and the Brewster mode (fields predominantly in the ITO layer) begin to separate as they are redshifted. The redshift is so significant that tracking changes in these modes required changing the experiment to a non-degenerate pump-probe setup so that the signal pulse used to observe the resonance dip in reflection could be spectrally offset from the pump pulse.

For this work, I developed a numerical model using transfer-matrix methods to investigate the conditions under which the Brewster mode in ITO is excited, hybridizes with the cavity modes, and how optical pumping redshifts both modes. Theng-Loo wrote the first draft, which I then modified. This draft is currently undergoing correction from all the co-authors in preparation for submission. My contributions to the work are summarized below:

1. Building, automating, and refining the experimental setup, including transferring to a non-degenerate pump-probe measurement setup (primary contributor alongside Theng-Loo Lim).
2. Performing the linear and nonlinear optical experiments and collecting the data (primary

contributor alongside Theng-Loo Lim).

3. Numerical modeling to explain the relative redshifting of different cavity modes (Primary contributor, with advice from Dr. Zahirul Alam)
4. Preparing the first draft of the manuscript (primary contributor alongside Theng-Loo Lim and Dr. Jeremy Upham).
5. Revising the manuscript (all authors).

The attached manuscript and supplementary information are prepared for submission and will be submitted after final revisions.

Ultrafast Dynamics of the Excitation of a Brewster Mode in an Epsilon-Near-Zero-Based Nanocavity

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Engineering large optical field enhancements to enhance light-matter interaction is a core strategy for developing practical nonlinear devices, whether for all-optical switches, quantum light sources, or enhanced sensors. Epsilon-near-zero (ENZ) transparent conductive oxides, such as indium tin oxide, not only show large nonlinear optical responses, but as thin films also possess ENZ modes capable of large field enhancements. Because such ENZ modes lie below the light line on a plot of frequency versus wave number, they require deliberate coupling techniques, such as metasurfaces, to access from free space, but above the light line, the Brewster mode also provides an opportunity for nonlinear enhancement and mode engineering. In this work, we demonstrate an epsilon-near-zero (ENZ) nanocavity by hybridizing such a Brewster mode with an étalon-type cavity mode. This hybrid mode not only provides field enhancement in the ITO layer but also enables dynamic control over the structure's reflectance. Time-resolved femtosecond pump-signal measurements, in which the signal is delayed with respect to the pump, reveal a pump-induced redshift of the hybrid mode from 1140 nm to 1310 nm, corresponding to a 170-nm spectral shift and a modulation depth of 25 dB. The switching occurs on a sub-picosecond timescale (~ 200 fs rise time and ~ 400 fs fall time). Much as grating couplers enabled harnessing the ENZ mode, our results show that coupling the Brewster mode to a cavity resonance can harness its nonlinear optical response and could serve as a promising platform for CMOS-compatible ultrafast all-optical switching.

I. INTRODUCTION

Enhancing light-matter interaction at the nanoscale is central to the development of ultrafast all-optical switching, efficient nonlinear frequency conversion, quantum light sources, and optical sensing[1–5]. One approach has been to harness epsilon-near-zero (ENZ) materials, materials for which the permittivity vanishes over a specific wavelength range, as they exhibit significant field enhancement, strong optical nonlinearities and fast material response times [6, 7]. Although many materials exhibit ENZ behavior, transparent conducting oxides (TCOs) are particularly valued because their ENZ wavelength range typically lies between 800 nm and 2500 nm[6–8]. Furthermore, TCOs are CMOS-compatible and can be integrated with silicon photonic devices; they are transparent in visible light; and have a high optical damage threshold (~ 1 TM/cm²). Indium tin oxide (ITO) is a TCO that is intensively used for optical nonlinear experiments [6, 9, 10], demonstrating optical Kerr-like changes of refractive index (Δn) up to 170% of its linear refractive index [9]. Such a large Δn makes it an ideal platform for realizing the time-refraction effect [11–13].

Furthermore, a sufficiently thin TCO film will also support a pair of plasmon modes close to its plasma

frequency, exhibiting significant enhancement of the E_z field component within the film, where z denotes the surface-normal direction [6, 14–18]. One is a Brewster mode, which is a transverse magnetic (TM) leaky mode for which the resonance condition is determined by the vanishing Fresnel reflection coefficients at oblique incidence[19, 20]. At its resonance condition, the Brewster mode will provide field enhancement inversely proportional to the film thickness (akin to the Berreman modes for surface phonon polaritons[21]), and is limited by the intrinsic material loss ($\text{Im}(\epsilon)$). Given that it can be excited from free space at oblique angles of incidence, its dispersion relation lies within the light cone (i.e., to the left of the light line in the frequency-in-plane wavevector diagram) [15]. There is also an ENZ mode that shows a large field enhancement inversely proportional to the film thickness[17], but as it lies to the right of the light line, it can only be accessed by a high-index prism in the Kretschmann configuration [14] or by grating couplers[22, 23]. Plasmon modes in ENZ materials can achieve ultrafast all-optical switching [14, 15, 24–26], polarization manipulation [15], enhanced four-wave mixing [27], and strong coupling between plasmon modes [28–30].

However, the limitation of the plasmon modes is that the material thickness must be deeply subwavelength (typically $d < \lambda_{\text{ZE}}/50$ [6, 7, 17, 21, 31]) for the modes to maintain high field enhancement. Otherwise, a Brewster-like mode can still couple to the film at its Brewster angle,

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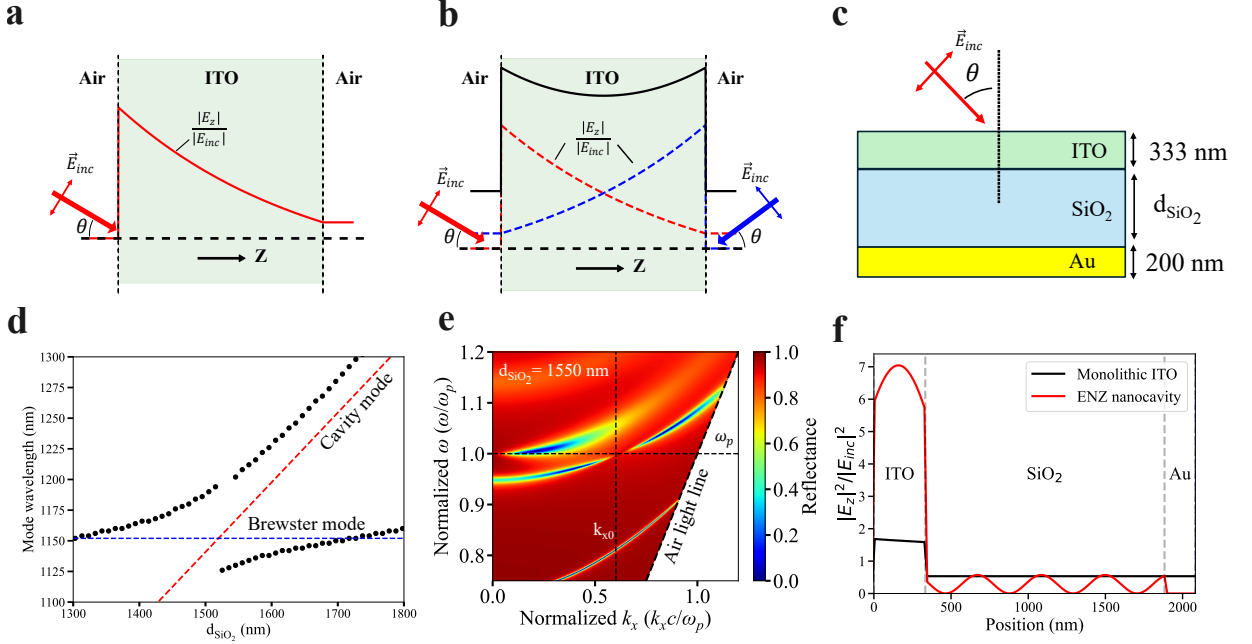


FIG. 1. **Proposed ENZ nanocavity and the induced Brewster hybrid mode.** **a**, A single incident beam interacts with an ITO film at an oblique angle θ . The electric field decays exponentially along the film thickness (z denotes the surface-normal direction). **b**, Two counter-propagating beams interact with the ITO film. For an appropriate relative phase, the fields interfere constructively, resulting in a non-decaying field profile within the film (black line). **c**, Schematic of the ENZ nanocavity. The thicknesses of the ITO and Au layers are fixed at 333 nm and 200 nm, respectively, while the SiO₂ spacer thickness d_{SiO_2} is varied. **d**, TMM-calculated mode wavelengths as a function of spacer thickness d_{SiO_2} . Two distinct modes are observed, corresponding to the cavity and Brewster modes. The black dots indicate the hybrid modes formed through their coupling, with optimal coupling at $d_{\text{SiO}_2} \approx 1550$ nm. **e**, TMM-calculated reflectance dispersion for p-polarized (TM) light in the ENZ nanocavity at $d_{\text{SiO}_2} = 1550$ nm, shown as a function of normalized frequency (ω/ω_p) and normalized in-plane wavevector ($k_x c/\omega_p$). Here ω_p is the plasma frequency of ITO, k_{x0} corresponds to an incident angle of 40°, and c is the speed of light in vacuum. **f**, The E_z field profile of the ENZ nanocavity ($d_{\text{SiO}_2} = 1550$ nm) as a function of position at an incident angle of 40° and a wavelength of 1100 nm (red line). For comparison, the field profile of a monolithic ITO film is also shown (black line).

θ , but the $|E_z|$ component of the field falls off exponentially, as illustrated for ITO in Fig. 1a. Because a nonlinear optical response is proportional to both the field enhancement and the interaction length within the nonlinear medium, this leads to an optimal thickness for a nonlinear device and a limit on its efficiency.

In this work, we consider how to restore the field enhancement of the Brewster-like mode for a thicker layer. If an additional beam were incident from the opposite side of the sample with the correct phase conditions, the fields would interfere constructively to produce a nearly uniform field distribution throughout the film (Fig. 1b). This approach maximizes the optical nonlinearity, as the entire volume of the ENZ film experiences stronger field enhancement. To create this pair of constructively interfering fields, we can simply let the ENZ film act as the partially reflective plate in a Gires-Tournois étalon such that the Brewster-like mode matches a cavity mode. The resulting Brewster hybrid mode would provide a more efficient nonlinear optical response than an equivalent ENZ thin film, either in transmission or in reflection on a reflective substrate [32], and could be readily characterized by simple reflection measurements.

We designed a multilayer stack consisting of a relatively thick ITO film (333 nm) of known spectral properties (the linear optical permittivity of this ITO is shown in Supplementary Note 1), a glass spacer, and a gold (Au) film, shown schematically in (Fig. 1c). This Gires-Tournois étalon—hereafter referred to as an ENZ nanocavity—supports multiple cavity modes, one of which could overlap with the Brewster-like mode in the ITO film. The cavity mode provides the coherently interacting reflected beam, resulting in constructive interference that drives the formation of the Brewster-hybrid mode.

II. TRANSFER MATRIX METHOD FOR NANOCAVITY DESIGN

Calculating the cavity mode wavelength at the incident angle of 37° as a function of the spacer thickness determines where this mode and the Brewster mode (at the ITO ENZ-crossing wavelength) will cross and thus achieve optimal coupling between them (Fig. 1d). Transfer matrix method (TMM) simulations of the resulting

hybrid modes (black dots) show strong interaction for d_{SiO_2} between 1500 nm and 1600 nm, indicating hybridization between the modes. However, to clearly resolve the mode behavior, these initial simulations assumed a ten-fold reduction in the ITO optical loss (Supplementary Note 2). Further analysis of the TMM simulations is provided in Supplementary Note 3. Based on these simulation results, a d_{SiO_2} thickness of 1550 nm was selected as optimal for the Brewster hybrid mode.

The corresponding p-polarized reflectance dispersion as a function of the normalized wavevector ($k_x c / \omega_{\text{ENZ}}$) and normalized frequency ($\omega / \omega_{\text{ENZ}}$) for this nanocavity above the light line is presented in Fig. 1e, where ω_{ENZ} corresponds to the epsilon-near-zero frequency of our ITO sample. The dispersion above the light line of the resulting modes provides insight into the anticipated reflectance properties of the device (Fig. 1e). To show that the field in the nanocavity enhances the field the field profiles for the ENZ nanocavity (red) and monolithic ITO (black) as functions of position in Fig. 1f, where a fourfold intensity enhancement is observed in the ENZ nanocavity.

Following the above design specifications, the fabricated ENZ nanocavity, consists of a 333 nm-thick ITO film, a SiO_2 spacer layer with a spacer thickness of d_{SiO_2} , and a 200 nm-thick gold (Au) film that acts as a back reflector. As expected, the ITO film on its own exhibits a relatively high reflectivity at its ENZ region and acts as a partial mirror with a dip in reflection at the Brewster mode.

Next, we experimentally confirm the existence of the Brewster hybrid mode. As a comparative reference, we performed TMM simulations of the linear reflectance of the ENZ nanocavity using ITO's actual optical loss over the observable spectral and angular range (Fig. 2a). This reflectivity response is qualitatively analogous to the dispersion curves of (Fig. 1e). The Brewster hybrid mode is thus expected to be clearly visible as a dip in reflection for an incident angle of 40° and near 1130 nm. The measured linear reflectance of a thermal light source incident on the sample at 40° is shown in Fig. 2b with the Brewster hybrid mode at 1138 nm. As expected, the experimental and TMM-simulated reflectance spectra are in good agreement, with slight discrepancies attributed to coupling losses and experimental imperfections. It is worth noting that the fourth-order cavity mode hybridizes with the Brewster mode, as shown in Fig. 1f. Furthermore, the resonance modes observed at 980 and 1540 nm correspond to the third- and fifth-order cavity modes, respectively.

III. STRENGTH OF NONLINEARITY IN THE ENZ NANOCAVITY

As ITO exhibits a large, nonlinear Kerr-like response with sub-ps response time, a pump-signal investigation of the cavity dynamics of the Brewster hybrid mode would

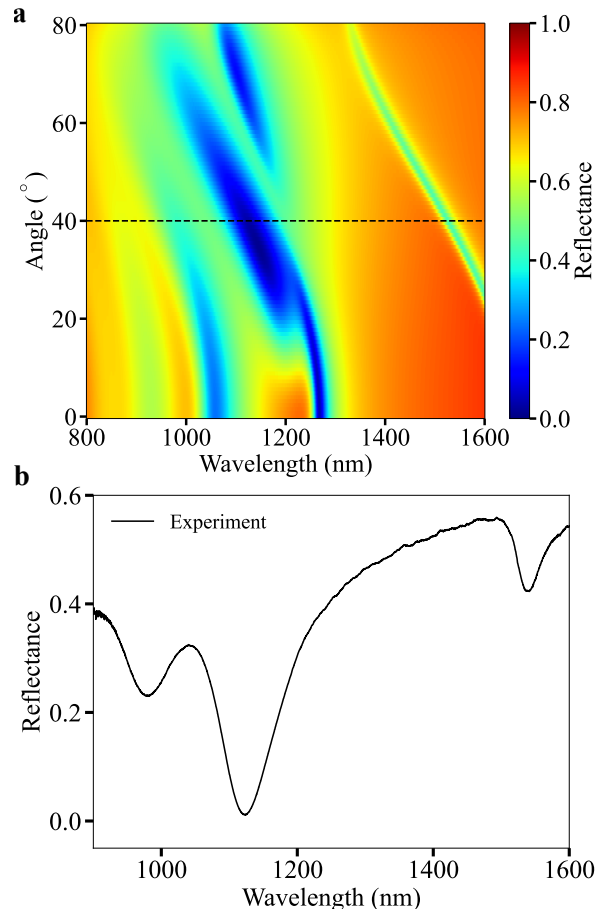


FIG. 2. Linear optical properties of the ENZ nanocavity. **a** Simulated linear reflectance of the ENZ nanocavity as a function of incident angle ($^\circ$) and wavelength (nm). **b** The experimental linear reflectance spectrum of the nanocavity as a function of wavelength (nm) at the incident angle of 40° . The Brewster hybrid mode is located at 1138 nm.

be a good indicator of field enhancement in ITO. Under intense pump excitation, conduction-band electrons are excited and redistributed by light-induced heating. Since ITO has a non-parabolic conduction band, this redistribution increases the effective mass of the electrons, leading to a significant redshift of the plasma frequency, consequently modifying the resonant wavelength of the Brewster hybrid mode[33]. To investigate the temporal dynamics and mode-shifting of the Brewster hybrid mode, we directed an intense pump pulse onto the sample at an angle of incidence of 30° , which is the incident angle closest to the Brewster hybrid mode (Fig. 3a, inset), while a weak signal pulse probed the hybrid mode near its resonance.

The pump-signal experiments were performed using a Ti: Sapphire laser to generate ~ 100 fs pulses at 800 nm, and the signal and pump wavelengths were tuned to the ENZ region of the sample using two optical parametric amplifiers (OPAs). These two beams were then sent into the signal and pump paths. We controlled the power of

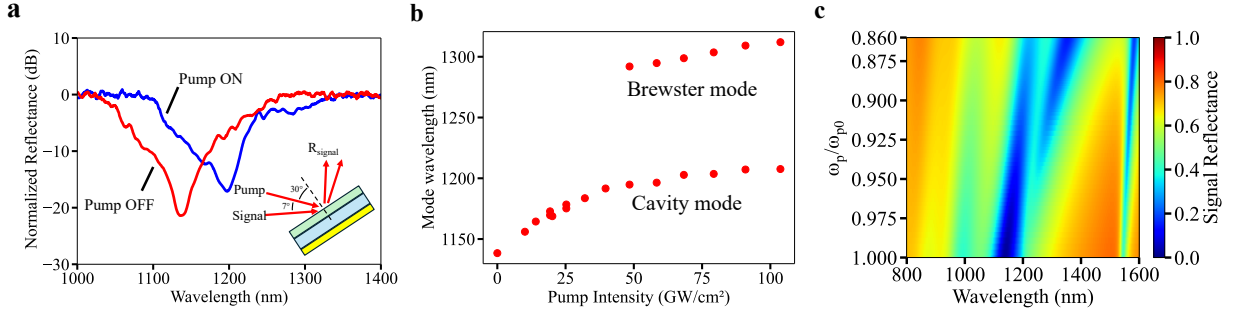


FIG. 3. Brewster and cavity mode shifting. **a**, Measured reflectance spectra without the pump (red) and under a pump intensity of 50 GW/cm² (blue). The inset provides a schematic of the experimental setup for the pump-probe measurements of the Brewster-hybrid mode. The pump and signal beams are incident on the sample at 30° and 37°, respectively. **b**, Experimental mode shift as a function of pump intensity. Both the cavity and Brewster modes are initially at 1138 nm. As the pump intensity increases, the Brewster mode redshifts to 1315 nm, while the cavity mode shifts to 1200 nm. **c**, TMM-simulated reflectance at an incident angle of 37°, plotted as a function of wavelength and the plasma frequency ratio (ω_p/ω_{p0}) of the ITO layer.

each beam using half-wave plates and Glan–Taylor polarizers and ensured both beams were p-polarized. By adjusting a translational stage in the signal path, we varied the delay time, $\Delta\tau$, between the pump and signal pulses. We set both beam spot sizes on the sample to 63 μm and maintained a signal intensity of 1.5 GW/cm² to avoid signal-induced optical nonlinearities. Meanwhile, we varied the pump intensity from 1 to 100 GW/cm². We directed the pump and signal beams onto the sample at angles of 30° and 37°, respectively, allowing them to interact with the Brewster hybrid mode of the ENZ nanocavity and enabling us to observe frequency shifting of the Brewster hybrid mode.

Because the signal pulse duration is approximately 100 fs and centered at 1130 nm, it has a finite spectral bandwidth extending roughly from 1110 nm to 1150 nm. The pulses are close to, but not strictly, transform-limited. Over this bandwidth, the reflection acts as a spectral window that samples the cavity resonance, which shifts significantly under excitation. The signal pulse reflections, normalized by the reflection from a silver mirror, are shown in Fig. 3a. In the absence of a pump, we can still locate the Brewster hybrid mode at 1130 nm. However, when the pump and signal are temporally overlapped ($\Delta\tau = 0$ fs), we can clearly observe the redshift of the Brewster hybrid mode to 1200 nm at a pump intensity of 50 GW/cm². To map out the redshift of the Brewster hybrid mode, we scanned the signal wavelength from 1130 nm to 1300 nm, while the pump wavelength is fixed at 1300 nm, and extracted the spectral locations of the modes as a function of pump intensity (Fig. 3b). We clearly observe that the Brewster-hybrid mode redshifts significantly in the presence of the pump, confirming a clear nonlinear optical response of this mode. Furthermore, the mode’s redshift appears to saturate at pump intensities near 50 GW/cm², which is significantly roughly half the saturation intensity we have observed for similar ITO layers in transmission under similar experimental conditions, this is at least suggestive that the field en-

hancement in the Brewster hybrid mode is higher than in the transmission case (recall Fig. 1f)). Perhaps most significantly, at pump intensities above 50 GW/cm², the hybrid mode splits into two distinct modes.

To explain the mode splitting phenomenon, we consider how the pump pulse alters the optical response of the entire ENZ-nanocavity system. The splitting is driven by the fact that the refractive index change (Δn_{ITO}) has a smaller impact on the cavity mode than on the Brewster mode. Because the change in the effective optical path length occurs primarily within the ITO layer rather than across the entire cavity (≈ 1500 nm), the cavity mode remains relatively stable. Conversely, the Brewster mode is strongly sensitive to Δn_{ITO} , resulting in a significantly larger shift that eventually decouples the two modes. Although the observed splitting is a dynamic response, we approximated it using TMM simulations of a static cavity under different ITO conditions. We varied the plasma frequency ratio (ω_p/ω_{p0}) of ITO from 1 to 0.85 and simulated the resulting change of the reflectance as a function of ω_p/ω_{p0} as a color map in Fig. 3c. Quantitatively, the TMM-calculated mode shifting is in good agreement with the experimental results (Fig. 3b). The simulation also captures mode splitting when $\omega_p/\omega_{p0} > 0.95$, where both modes redshift at different rates.

In Supplementary Note 4, we present two additional TMM simulations to demonstrate that the modes redshift at different rates: (1) a TMM simulation with an s-polarized beam using the same nanocavity dimensions, and (2) a TMM simulation with a p-polarized beam for the ENZ nanocavity without a spacer. Case 1 contains only the cavity mode, while Case 2 contains only the Brewster mode. As the plasma frequency changes, these two modes clearly redshift at different rates, leading to the observed mode splitting.

IV. TEMPORAL DYNAMICS OF THE ENZ NANOCAVITY

We next investigated the temporal dynamics of the Brewster-hybrid mode by varying the pump-signal delay time ($\Delta\tau$), with the pump wavelength fixed at 1300 nm and the signal wavelength set to 1130 nm (to act as a spectral window observing how the Brewster-hybrid mode begins redshifting) and to 1300 nm (to observe where the Brewster mode arrives after redshift). Also, the pump and signal intensities are fixed at 100 and 1.5 GW/cm², respectively. The normalized reflected spectral amplitudes are plotted as functions of $\Delta\tau$ and wavelength in Fig. 4.

When the signal wavelength is centered at 1130 nm as shown in Fig. 4a, the Brewster hybrid mode undergoes a red shift from 1138 nm as $\Delta\tau$ increases from -200 fs to 0 fs. It then takes ≈ 400 fs for the mode to return to its original spectral position. This is consistent with the relaxation time in ITO, which is attributed to electron-phonon interactions and typically occurs on a sub-picosecond timescale [9]. The spectra at each $\Delta\tau$ time step of Fig. 4a are individually normalized to best illustrate the spectral variations. Next we consider the overall change in reflected signal power for the same experimental conditions, normalized to the peak reflectance (Fig. 4b), which shows a clear increase as the Brewster hybrid mode redshifts away, but a return to nearly the same reflectance value at about 400 fs, consistent with the blueshift of the Brewster hybrid mode. To capture the time dynamics of overall signal reflectance, we used a dynamic model developed by Bohn et al. [14], which describes time-modulated reflectance via a time-dependent permittivity. This model defines the ITO response as the convolution of the pump pulse with an exponential decay associated with electron-phonon relaxation (see Supplementary Note 5). The model successfully captures the time-varying features of the mode at a signal wavelength of 1130 nm (Fig. 4c).

We similarly investigate the temporal dynamics at the signal wavelength to 1300 nm (Fig. 4d-f). Figure 4d displays the normalized reflectance spectrum as a function of $\Delta\tau$, where the Brewster mode is clearly shifted to 1300 nm between -200 fs and 0 fs before rapidly disappearing as $\Delta\tau$ exceeds 0 fs. The corresponding reflectance in Fig. 4e shows an opposite trend to that in Fig. 4b: as the Brewster-hybrid mode approaches the signal wavelength, absorption increases, leading to a sharp decline in reflectance. These time-varying features are also accurately reproduced by the dynamic model (Fig. 4f).

To quantify the potential of this dynamic Brewster hybrid mode as a possible optical switch, Supplementary 6 rescales the spectra of Figs. 4a to show a modulation of up to 25 dB at 1130 nm with a switch-on time of 200 fs and a switch-off time of roughly 400 fs. This is a proof-of-principle demonstration of rapid modulation of Brewster-like modes in a TCO film that could function as

sub-ps gates or sudden-onset power dampeners for safety applications.

V. CONCLUSION

In conclusion, we designed and fabricated an ENZ nanocavity that supports both Brewster and étalon-type cavity modes. By engineering the spacer thickness of the nanocavity, these modes couple to form a Brewster hybrid mode, providing greater field enhancement and thus greater dynamic nonlinear optical responsiveness. To study this hybrid mode, we performed pump-intensity and time-resolved pump-signal experiments and obse. We observed Brewster hybrid mode redshifted and split, with the Brewster mode component shifting from 1130 nm to 1315 nm, a 170-nm shift. The reflectance at the initial resonance wavelength changed by 25 dB, while the attenuation at the destination resonance wavelength decreased by 15 dB. The switching onset occurs roughly 200 fs after electron intraband excitation, followed by sub-picosecond recovery, likely governed by electron-phonon relaxation. Future optimization of the Brewster hybrid modes for larger switching amplitudes or their integration with plasmonic or dielectric metasurfaces to enable additional degrees of freedom, such as dynamic polarization modulation, would further expand the functionality of ENZ-based photonic devices[34, 35].

Sample fabrication

The ENZ nanocavity samples were fabricated by sequential thin-film deposition on glass substrates. A 330-nm-thick ITO film is deposited as the front partial mirror and nonlinear active layer, followed by SiO₂ spacer layers of either 1500 nm (High-Q) or 100 nm (Low-Q) thickness. Finally, a 200-nm-thick Au layer was deposited as the back reflector. Film thicknesses and optical constants were characterized by spectroscopic ellipsometry.

Optical characterization

Linear reflectance spectra were measured using a white-light source with angle-resolved detection for TM-polarized light. The optical permittivity of the ITO films was extracted from ellipsometry measurements and fitted with a Drude model to determine the ENZ wavelength.

Transfer matrix method simulations

Reflectance spectra and field distributions were calculated using the transfer-matrix method with measured optical constants for each layer, following the description in Ref.[36]. Pump-induced changes were modeled by varying the plasma frequency of the ITO Drude model.

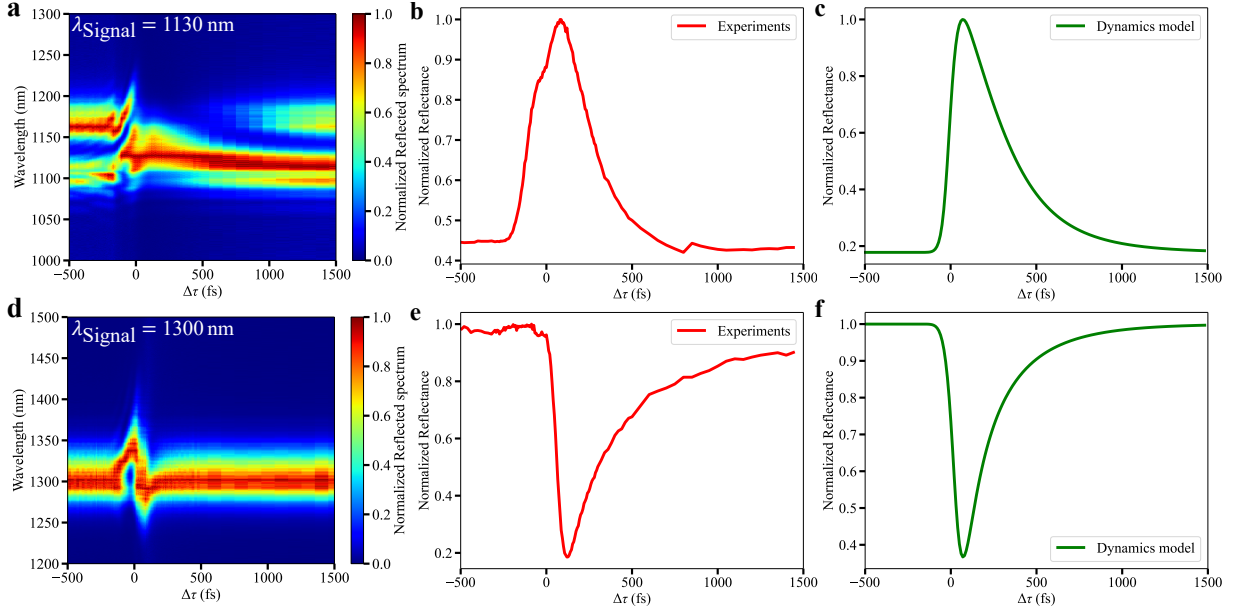


FIG. 4. **Time dynamics of the Brewster hybrid mode in a pump-signal configuration.** **a**, Measured reflectance spectrum as a function of wavelength and delay time ($\Delta\tau$) for a signal centered at 1130 nm. **b**, Experimental and **c**, calculated normalized signal reflectance at 1130 nm. **d-f**, Corresponding results for a signal wavelength of 1300 nm, showing **d**, the full reflectance spectrum, **e**, experimental transients, and **f**, calculated transients. For all panels, the pump wavelength is fixed at 1300 nm at an intensity of 100 GW/cm^2 .

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGEMENT

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AUTHOR CONTRIBUTIONS

M.Z.A. and R.A. conceptualized the experiment and designed the sample. Y.V., T.L., and M.Z.A. initiated the experimental work. Y.V. and T.L. performed all measurements, analyzed the data, and developed numerical models, assisted by J.U. and M.Z.A. S.V. and J.R.H. fabricated the samples. Y.M. and R.M.C.C. built the linear measurement setup. Y.V. and T.L. wrote the initial draft. All authors discussed results and contributed to manuscript preparation. J.U., M.Z.A., R.M.C.C., and R.W.B. supervised the project.

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Supporting Information: Ultrafast Dynamics of the Excitation of a Brewster Mode in an Epsilon-Near-Zero-Based Nanocavity

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I. SUPPLEMENTAL NOTE 1: LINEAR OPTICAL PERMITTIVITY OF ITO FILM

The real and imaginary parts of the optical permittivity for the ITO film used in the ENZ nanocavity were experimentally obtained by ellipsometry. We then employed the Drude model to extract the linear optical parameters, including the plasma frequency ($\omega_p = 3.098 \times 10^{15}$ rad/s), the damping rate ($\gamma = 1.025 \times 10^{14}$ s⁻¹), and the background permittivity ($\epsilon_\infty = 3.908$). The fitting results are shown in Figure S1, confirming that the ENZ wavelength of this sample is 1200 nm.

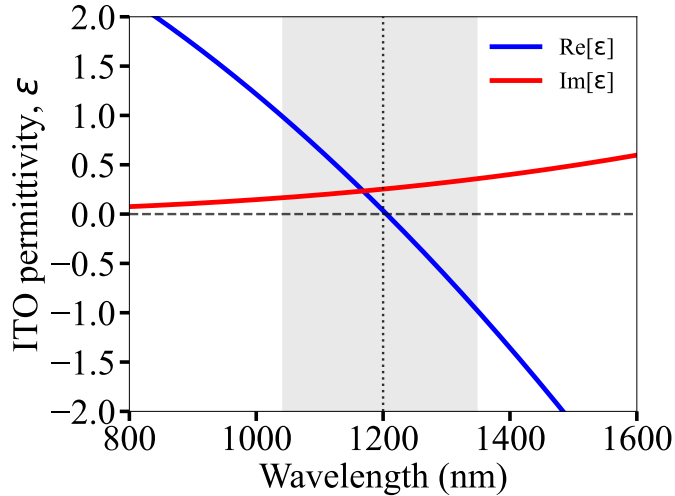


FIG. S1. **Optical permittivity of ITO** The real (blue) and the imaginary (red) parts of ITO permittivity as a function of laser wavelength. The ENZ wavelength of this sample (λ_{ENZ}) is 1200 nm.

II. SUPPLEMENTAL NOTE 2: BREWSTER AND CAVITY MODE MANIPULATION BY TUNING SPACER THICKNESS

To determine the optimal spacer thickness for the Brewster hybrid mode, we performed a series of TMM calculations by varying d_{SiO_2} from 0 nm to 1550 nm, and the resulting simulated dispersion plots are shown in Fig. S2. Initially, we observe a single mode (Brewster mode) at $d_{\text{SiO}_2} = 0$ nm, which appears near the plasma frequency (ω_p) of ITO. As d_{SiO_2} increases, a cavity mode emerges because the ITO layer acts as an effective mirror; simultaneously, the Brewster mode undergoes a spectral shift.

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Interestingly, at $d_{\text{SiO}_2} = 1550$ nm, we observe that the induced cavity mode hybridizes with the Brewster mode at ω_p . This interaction suggests a coupling between the Brewster and cavity modes. Consequently, we selected a spacer thickness of $d_{\text{SiO}_2} = 1550$ nm for our ENZ nanocavity to determine this coupled state.

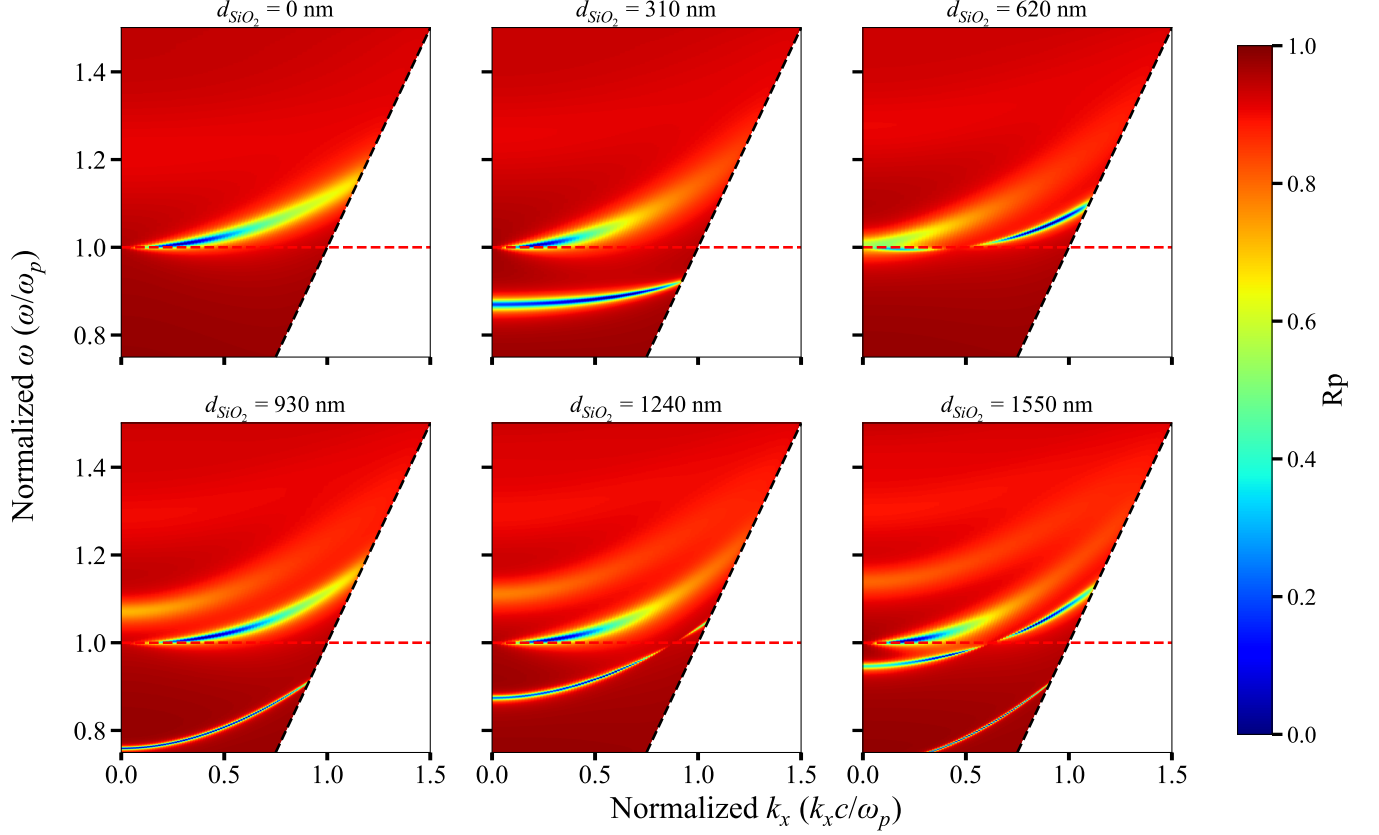


FIG. S2. **Brewster and cavity mode manipulation by tuning spacer thickness of the ENZ nanocavity** The calculated dispersion relation of the ENZ nanocavity with various spacer thickness, d_{SiO_2} .

III. SUPPLEMENTAL NOTE 3: MODE COUPLING IN ENZ NANOCAVITY

To demonstrate the coupling between the Brewster and cavity modes, we performed three distinct TMM calculations: (1) an ENZ nanocavity with $d_{\text{SiO}_2} = 1550$ nm under s-polarized light; (2) an ENZ structure without a spacer ($d_{\text{SiO}_2} = 0$ nm); and (3) an ENZ nanocavity with $d_{\text{SiO}_2} = 1550$ nm under p-polarized light. The resonant wavelengths for each case were extracted and plotted as a function of the angle of incidence in Fig. S3.

Initially, we observe that the cavity modes for s-polarized (blue circles) and p-polarized light (red crosses) align closely at shorter wavelengths (< 1200 nm), as these modes are largely insensitive to polarization in this regime. At longer wavelengths, however, the modes begin to diverge due to Fresnel effects in ITO at oblique angles of incidence.

As the wavelength approaches the ENZ region of the ITO, the Brewster mode supported by the ITO-Au stack (green triangles) overlaps with the cavity mode at an incident angle of 40° . This overlap suggests a coupling between the two modes. It is worth noting that, without the spacer (Case 2), no cavity modes are supported, leaving only the Brewster mode.

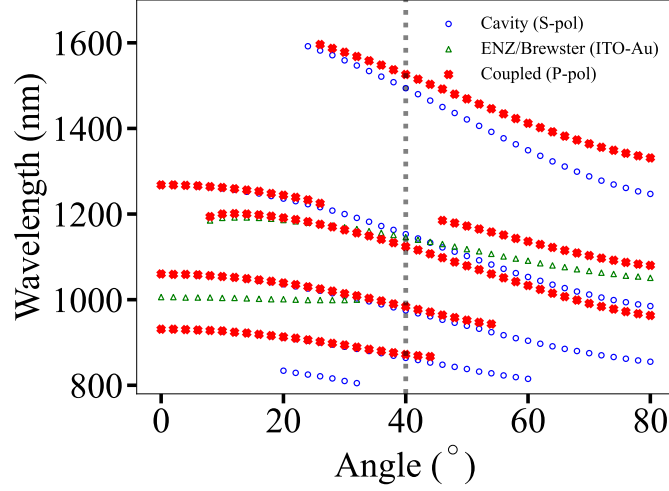


FIG. S3. **Mode coupling in ENZ nanocavity** Comparison of optical modes calculated via TMM for three configurations: (1) an ENZ nanocavity with $d_{\text{SiO}_2} = 1550$ nm under s-polarized light (blue circles); (2) an ENZ structure without a spacer ($d_{\text{SiO}_2} = 0$ nm) showing the intrinsic Brewster mode (green triangles); and (3) an ENZ nanocavity with $d_{\text{SiO}_2} = 1550$ nm under p-polarized light (red crosses). A clear resonance overlap is observed at an incident angle of 40° near the ENZ wavelength of ITO, suggesting mode coupling and hybridization in this configuration.

SUPPLEMENTAL NOTE 4: MODE SPLITTING WITH VARIOUS PLASMA FREQUENCIES

To demonstrate that our nonlinear experimental results exhibit the characteristic features of mode coupling between the Brewster and cavity modes, we performed two distinct TMM calculations by sweeping the plasma frequency of the ITO: (1) an ENZ nanocavity with $d_{\text{SiO}_2} = 1550$ nm under s-polarized light, and (2) an ENZ structure without a spacer ($d_{\text{SiO}_2} = 0$ nm).

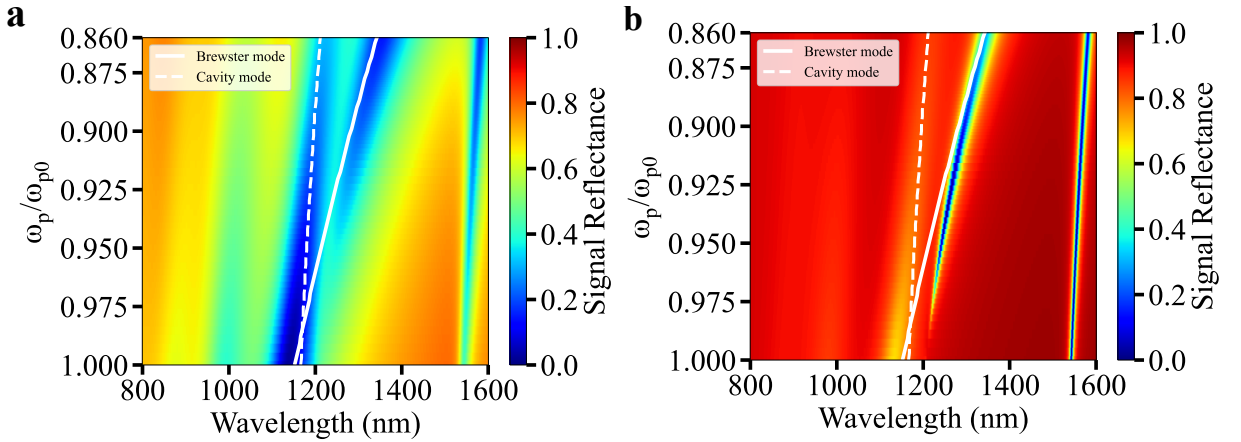


FIG. S4. **Mode coupling under plasma frequency tuning** Calculated resonant wavelengths for the Brewster mode (red solid line, $d_{\text{SiO}_2} = 0$ nm) and the cavity mode (red dashed line, $d_{\text{SiO}_2} = 1550$ nm under s-polarization). These are overlaid on p-polarized reflectance colormaps of the ENZ nanocavity ($d_{\text{SiO}_2} = 1550$ nm) as functions of wavelength and plasma frequency ratio. Simulations are shown for: **a**, the measured optical damping constant ($\gamma = 1.025 \times 10^{14}$ rad/s) and **b**, a reduced optical damping constant ($\gamma = 1.025 \times 10^{13}$ rad/s) to highlight the coupling dynamics.

The resonance wavelengths for each case—represented by a red line for the Brewster mode and red dots for the cavity mode—were extracted and overlaid on a reflectance colormap. These are plotted as functions of the plasma frequency ratio (ω_p/ω_{p0}) and wavelength. The experimental results (white dots) are compared against the simulations using both the actual measured loss of the ITO (1.025×10^{14} rad/s, Fig. S4a) and a low-loss case (1.025×10^{13} rad/s, Fig. S4b).

SUPPLEMENTAL NOTE 5: DYNAMIC MODEL

In this section, we discuss the dynamic model developed by Bohn et al. [1], which captures the transient change in reflectance driven by the time-modulated electric permittivity. The underlying logic of this model is illustrated in Fig. S5.

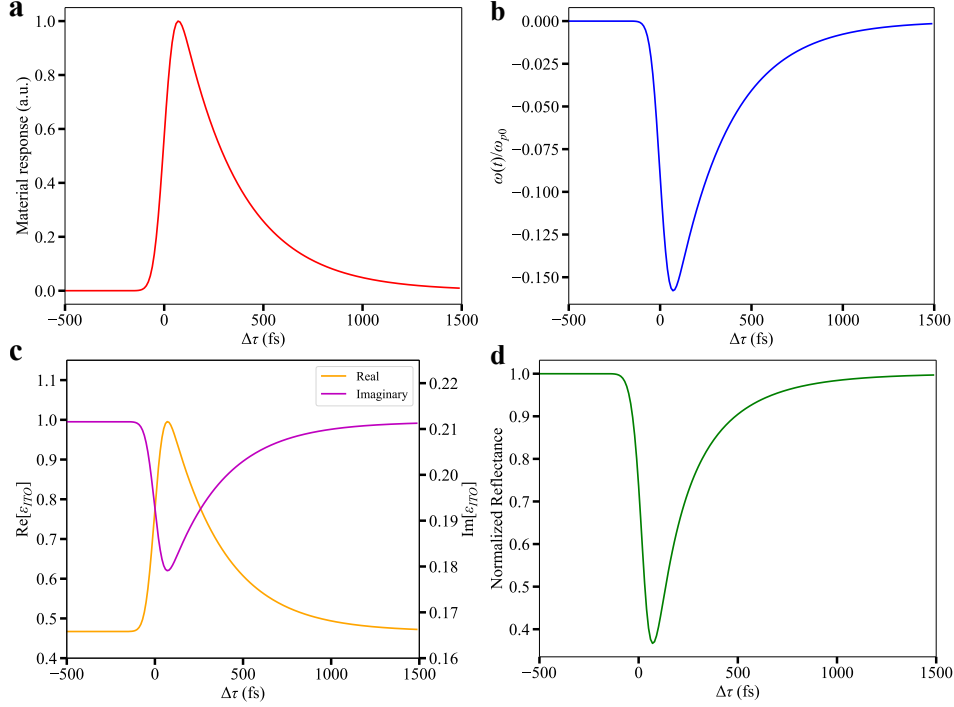


FIG. S5. **Basic logic of the dynamic model** Overview of the calculation flow used to determine the temporal dynamics of the ENZ nanocavity.

First, the model calculates the material response of ITO, defined as the convolution of the pump pulse (with a temporal pulse width of 100 fs) and an exponential decay associated with electron-phonon relaxation, with a response time of ~ 300 fs [2]. This process yields the material response as a function of the delay time, $\Delta\tau$ (Fig. S5a). Subsequently, this response is used to determine the temporal modulation of the plasma frequency, $\omega_p(\Delta\tau)$ (Fig. S5b), using a maximum plasma frequency shift ratio of $\omega_p/\omega_{p0} = -0.15$ [1].

Using the temporal change in plasma frequency, we then obtain the time-dependent real and imaginary parts of the ITO permittivity from the Drude model (Fig. S5c):

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (1)$$

Finally, the obtained real and imaginary parts of the electric permittivity are used in TMM calculations to determine the temporal reflectance as a function of $\Delta\tau$ (Fig. S5d).

To gain a full picture of the temporal dynamics of the Brewster-hybrid mode, we utilized the dynamic model to sweep the signal wavelength and delay time. The resulting signal reflectance is plotted as a function of wavelength and delay time ($\Delta\tau$) in Fig. S6. We can clearly observe that the Brewster and cavity modes experience distinct red-shifts, leading to a spectral separation between the two modes from 0 to 500 fs. Subsequently, both modes gradually merge back together after 500 fs as the system relaxes via electron-phonon interaction.

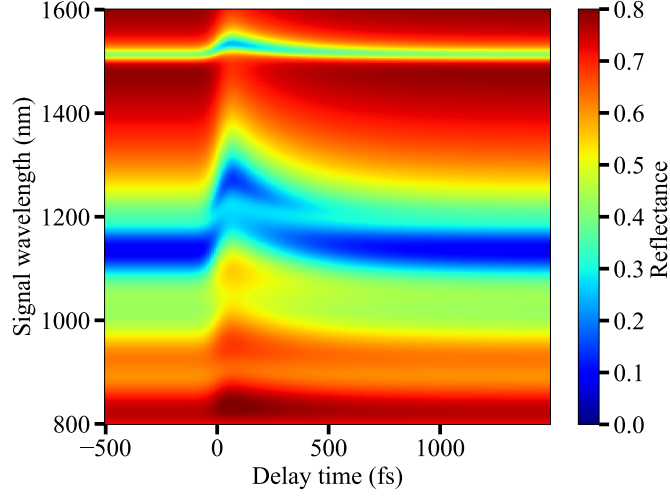


FIG. S6. **Dynamic model calculations of the ENZ nanocavity reflectance.** Calculated reflectance spectrum of the ENZ nanocavity as a function of signal wavelength (nm) and delay time (fs) using the dynamic model.

SUPPLEMENTAL NOTE 5: REFLECTANCE SPECTRA ON A DECIBEL SCALE

To evaluate the potential for ultrafast optical switching applications, we presented the same data from the main text in terms of optical density (OD) in Fig. S7a ($\lambda_{\text{Signal}} = 1130\text{nm}$) and Fig. S7b ($\lambda_{\text{Signal}} = 1300\text{nm}$), where OD is defined as $\text{OD} = -10\log_{10}(R_{\text{Pump}}/R_{\text{Linear}})$.

The device exhibits a switching time of approximately 200 fs, with observed changes in OD reaching -25 dB at a signal wavelength of 1130 nm. As shown in Fig. S7b, the Brewster mode shifts toward 1300 nm between -200 fs and 0 fs, resulting in a corresponding OD of -15 dB.

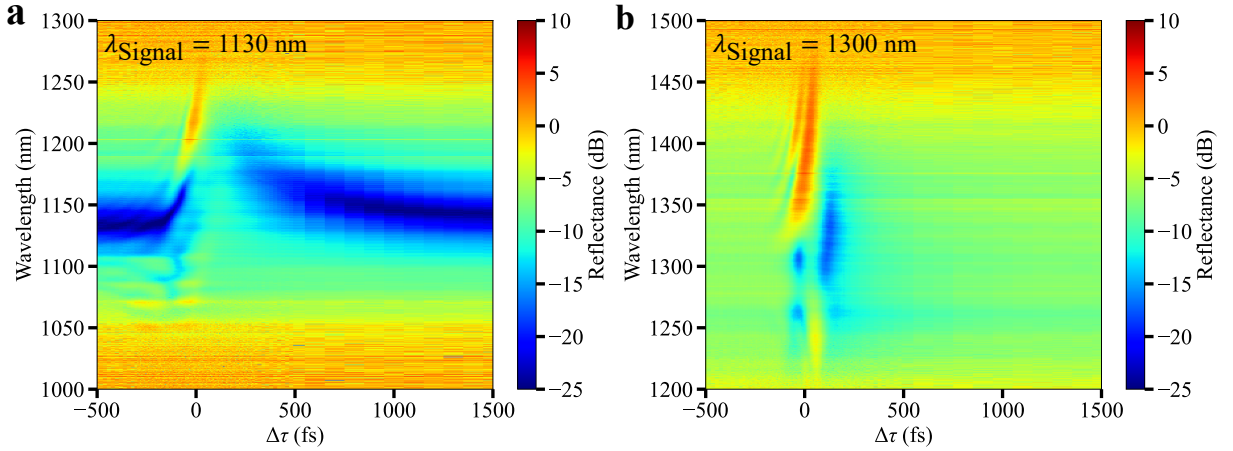


FIG. S7. **Optical switching using ENZ nanocavity.** The reflectance spectra as functions of wavelength (nm) and delay time (fs) in dB scale for signal wavelength of **a**, 1130 nm and **b**, 1300 nm.

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- [1] J. Bohn, T. S. Luk, C. Tollerton, S. W. Hutchings, I. Brener, S. Horsley, W. L. Barnes, and E. Hendry, All-optical switching of an epsilon-near-zero plasmon resonance in indium tin oxide, *Nature Communications* **12**, 1017 (2021).
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Chapter 4

Unity-order efficiency wave mixing in epsilon-near-zero nanostructures

Contribution Statement

This work follows directly from the experimental investigation described in Chapter 3. Here again, we are using the sample Gires-Tournois cavities, with one reflector being an ITO thin film, which was conceived by Dr. Zahirul Alam and Dr. Rasoul Alaei and fabricated by Dr. Shivashankar Vangala and Dr. Joshua R. Hendrickson. While aligning the pump-signal setup, I discovered that the four-wave mixing (FWM) signal was significantly brighter when either the pump or the signal was resonant with the cavity modes, compared to the bare ITO samples used in Chapter 2.

Theng-Loo and I then systematically measured the FWM output as a function of wavelength and incident angle, revealing a significant enhancement in FWM efficiency compared to bare ITO.

This observation motivated us to investigate the origin of the enhancement. Theng-Loo and I performed all the linear and nonlinear optical experiments under the supervision of Dr. Zahirul Alam. I developed a numerical model of the nanocavity using transfer-matrix methods to explain how field enhancement in the ITO layer, the cavity modes, and the hybridized modes contributed to the enhanced FWM response. The model was also used to study how these modes and field enhancements evolve as the plasma frequency of ITO is varied, analogous to changing the ITO refractive index under optical pumping.

I prepared the first draft of the manuscript, after which Theng-Loo took the lead in preparing subsequent drafts. The manuscript is currently undergoing revisions with input from all co-authors in preparation for submission.

My contributions to the work are summarized below:

1. Building, automating, and refining the experimental setup used to quantify the nonlinear response of the nanocavity (primary contributor alongside Theng-Loo Lim).
2. Performing the linear and nonlinear optical experiments and collecting the data (primary contributor alongside Theng-Loo Lim).
3. Numerical modeling to explain cavity field enhancement, mode hybridization, and the resulting enhancement in FWM efficiency (primary contributor, with advice from Dr. Mohammad Zahirul Alam and in consultation with co-authors).
4. Preparing the first draft of the manuscript (primary contributor).
5. Revising the manuscript (all authors).

The attached manuscript and supplementary information are prepared for submission and will be submitted after final revisions.

Unity-Order Efficiency Wave Mixing in Epsilon-Near-Zero Nanostructures

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Advances in metasurface technology have driven a decade-long search for a free-space, sub-wavelength-thick structure capable of high-efficiency nonlinear frequency mixing. Despite significant progress, metasurfaces made of conventional materials still yield efficiencies far below those of bulk crystals. Four-wave mixing (FWM)—a process underlying applications from frequency combs to entangled photon-pair generation—is typically on the order of 10^{-6} in such structures. Because FWM efficiency scales quadratically with the nonlinear interaction length, high conversion in conventional materials requires long propagation lengths. Transparent conducting oxides in their epsilon-near-zero (ENZ) regime offer a promising exception, but ENZ materials are lossy, and no practical loss-mitigation strategy has been demonstrated, which limits the field enhancement and the strength of nonlinear light-matter interactions. Here, we exploit a simple yet previously overlooked route to unity-order FWM efficiency: excitation of the Brewster mode in a 333 nm-thick indium tin oxide (ITO) film at its ENZ frequencies. We experimentally demonstrate an external FWM efficiency as high as $47.2 \pm 0.4\%$, enabled by the strong light-matter interaction of the Brewster mode in the ENZ film. This is comparable to the efficiencies reported for III-V waveguides, whose nonlinear interaction lengths are at least four orders of magnitude greater than ours. In fact, the nonlinear light-matter interaction in this structure is so strong that we observe up to the 12th-order wave mixing process. Our findings open routes to engineered metastructures with unity-order wave-mixing efficiencies, enabling free-space multimode signal processing with structured light, real-time holography, and quantum optics in wavelength-scale devices.

Four-wave mixing (FWM) is a parametric process in nonlinear optics that underlies numerous applications, including parametric amplification^{1, 2}, optical signal regeneration³, all-optical switching⁴, phase-sensitive amplification⁵, ultrafast metrology⁶, wavelength conversion for telecommunications⁷, and entangled photon-pair generation for quantum information⁸. In a FWM process, four photons interact through the third-order nonlinear susceptibility $\chi^{(3)}$ of a material. One such scheme involves two pump photons at frequency ω_{pump} and a signal photon at ω_{signal} interacting to generate an idler photon at $\omega_{\text{idler}} = 2\omega_{\text{pump}} - \omega_{\text{signal}}$ ^{9, 10}.

The conversion efficiency of FWM depends quadratically on the product of $\chi^{(3)}$, pump intensity, and interaction length, with maximum efficiency achieved under perfect phase-matching conditions. Consequently, traditional approaches to enhance FWM efficiency have focused on extending interaction lengths while confining light over smaller cross-sectional areas in waveguides^{1, 2, 11, 12} or exploiting enhanced interactions in high-quality-factor microring resonators¹³. In the frequency-degenerate case, the conversion efficiency scales with the fourth power of the intensity enhancement factor, while in the more general frequency-nondegenerate case it scales with the product of the intensity enhancements at the pump, signal, and idler fre-

quencies. However, these approaches introduce stringent requirements for dispersion management, advanced fabrication processes, and larger device footprints.

Plasmonic and metasurface nanostructures have emerged as alternative platforms that leverage extreme local field enhancement to boost nonlinear light-matter interactions in subwavelength volumes^{14–24}. While these structures benefit from relaxed phase-matching requirements due to their nanoscale dimensions, the achievable FWM efficiencies have remained modest, and plasmonic structures generally exhibit low damage thresholds, limiting the pump intensity. In recent years, a promising alternative has emerged in the form of semiconducting epsilon-near-zero (ENZ) materials — a class of materials where the real part of the dielectric permittivity approaches zero at specific wavelengths^{25–27}. In this regime, transparent conducting oxides, such as indium tin oxide (ITO), exhibit extraordinarily large and ultrafast optical nonlinearities, with refractive index changes exceeding $\Delta n \approx 0.72$ ^{26, 28, 29}. These materials are compatible with CMOS fabrication processes and operate at telecommunications wavelengths, making them attractive for integrated photonics. Previous demonstrations of FWM in 500-nm-thick aluminum zinc oxide in its ENZ regime were reported to be as large as 7%^{30, 31}. However, ENZ materials suffer from losses and, thus, the loss coefficient limits the propagation length. Thus, a solution that increases the external efficiency to the unity order for a given nonlinear optical process in a known ENZ material without increasing its thickness may turn out to

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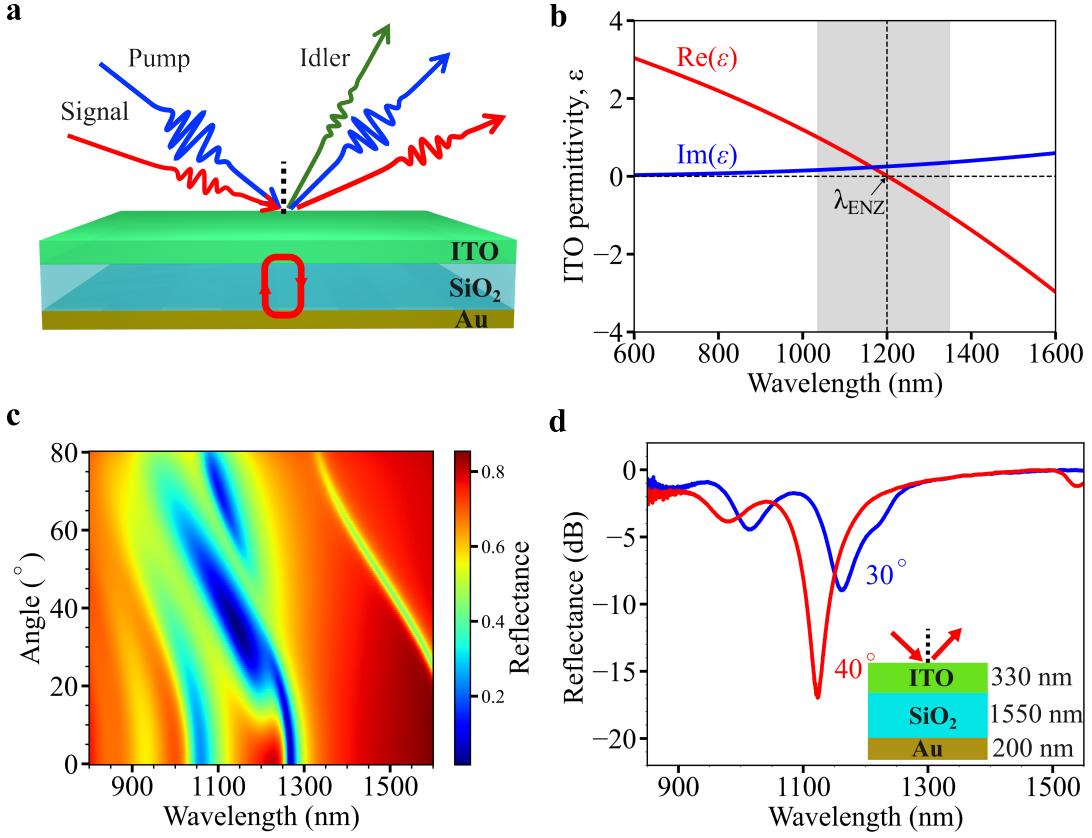


FIG. 1. **Design and linear optical properties of the ENZ nanostructure.** **a**, Schematic of the ENZ-based Gires-Tournois nanostructure comprising a 333-nm ITO film (partial reflector and nonlinear medium), SiO₂ spacer (1549 nm for High-Q, 101 nm for Low-Q samples), and 200-nm Au back reflector. The pump and signal beams are incident at 30° and 37°, respectively, with the idler generated at ~23° via the FWM process $\omega_{\text{idler}} = 2\omega_{\text{pump}} - \omega_{\text{signal}}$. **b**, Measured real (red) and imaginary (blue) parts of the ITO dielectric permittivity showing the ENZ wavelength at ~1200 nm. **c**, Calculated reflectance of the High-Q nanostructure for p-polarized light as a function of wavelength and angle of incidence, showing ENZ nanostructure resonances (dark bands) in the ENZ spectral region. **d**, Measured normalized reflectance spectra at 30° (blue) and 40° (red), confirming modes at 1161 nm and 1123 nm, respectively.

be technologically important for both classical nonlinear optics and, by extension, quantum processes such as spontaneous FWM. The unity order efficiency in classical FWM using such a nanostructure would imply the obtainable efficiency in SFWM as large as that which can be achieved using a bulk crystal⁸.

Here, we experimentally demonstrate an external FWM efficiency of $47.2 \pm 0.4\%$ using a simple three-layer structure: a 333-nm-thick ITO layer, a spacer layer, and a gold reflector layer (Fig. 1a). Such a structure allows simultaneous excitation of both the Brewster mode, which is localized in the ITO layer, and the Gires-Tournois etalon modes, which are distributed throughout the structure. The thick gold layer acts as a near-perfect back reflector, and the ENZ layer acts as a partial mirror due to its high impedance. The dielectric permittivity of the ITO film, measured by spectroscopic ellipsometry, shows a characteristic zero crossing of the real part of the permittivity at approximately 1200 nm (Fig. 1b).

RESULTS

The thickness of the spacer layer determines the resonance condition, in terms of both wavelength and wavevector, for the etalon modes. The excitation condition for the Brewster mode is more subtle. Conventionally, the Brewster mode of a film corresponds to the zero-reflection condition for p-polarized incident light. In a lossy material, however, the reflection does not vanish entirely. In the presence of a reflector, p-polarized light can nonetheless constructively interfere within the ITO layer. For near-normal incidence, constructive interference occurs near the wavelength of zero permittivity. As the transverse wavevector increases (i.e., at larger angles of incidence), the constructive interference condition shifts to wavelengths shorter than the zero-permittivity wavelength. Beyond a critical angle of incidence, the phase of the reflected wave undergoes a sign flip due to the change in the Fresnel coefficient of the air-ITO interface, and the mode ceases to be supported. This

constructive interference gives rise to strong electric-field enhancement within the ENZ film — a behavior that is fundamentally distinct from the etalon modes, whose resonance condition is primarily governed by the SiO₂ spacer thickness and whose resulting field enhancement is confined to the spacer layer. The interplay between the Brewster and etalon modes determines the structure’s linear optical response.

We employed transfer-matrix method (TMM) calculations to design and analyze the structures under study. Figure 1c presents the calculated reflectance spectrum for a 1549-nm SiO₂ spacer (designated the “High-Q” sample) as a function of wavelength and angle of incidence for TM-polarized (p-polarized) light. Details of the TMM calculations for the ITO film and the low-Q sample (SiO₂ spacer thickness of 101 nm) are provided in Supplementary Note 1. The dark bands indicate resonances at which light is efficiently coupled into the structure. We used a broadband thermal light source and spectrometer to measure the wavelength-dependent absolute linear reflectance of the structure. The measurements (Fig. 1d) show excellent agreement with the TMM predictions: the measured reflectance minima at 1161 nm (30°) and 1123 nm (40°) closely match the calculated resonance positions. We present the linear optical characterization of the low-Q sample in Supplementary Note 2. TMM simulations of the electric-field intensity distribution confirm that the field enhancement at these resonances is predominantly localized within the ITO layer — a configuration that is optimal for exploiting the ENZ nonlinearity (see Supplementary Note 1).

We conducted frequency-degenerate FWM measurements using a pump-signal configuration where both beams are at the same wavelength (Fig. 1a). The pump beam is incident at 30°, while the signal beam is incident at 37° so as to maximally couple to the Brewster modes and to exploit the associated intensity enhancements. A detailed experimental setup is shown in Supplementary Note 3. Energy conservation ($\omega_{\text{idler}} = 2\omega_{\text{pump}} - \omega_{\text{signal}}$) and momentum conservation along the surface ($k_{\text{idler}} \sin \theta_{\text{idler}} = 2k_{\text{pump}} \sin \theta_{\text{pump}} - k_{\text{signal}} \sin \theta_{\text{signal}}$) dictate that the idler emerges at approximately 23° in reflection. We define the FWM conversion efficiency as $\eta = P_{\text{idler}}(z = L)/P_{\text{signal}}(z = 0)$, i.e., the ratio of output idler power to input signal power.

Under intense optical pumping, the nonlinear modification of the ITO permittivity shifts the ENZ wavelength, thereby redshifting the resonances³². The Brewster mode is strongly confined within the ITO layer, so its resonance position is significantly more sensitive to the pump-induced permittivity change than the etalon modes, which are predominantly localized within the SiO₂ spacer. To numerically understand this pump-induced resonance shift, we performed TMM simulations in which the plasma frequency of the ITO permittivity was varied, corresponding to the nonlinear refractive-index change in ITO (Δn up to 0.72). The resulting reflectance maps show the evolution of the nanostruc-

ture resonances as a function of wavelength and plasma-frequency shift (Supplementary Note 4). At high pump intensities, the Brewster mode shifts toward ~1300 nm, motivating the choice of operating wavelength for the DFWM measurements.

Figure 2a shows the measured idler efficiency as a function of pump intensity for a pump-signal wavelength of 1300 nm. The efficiency shows the expected quadratic dependence on pump intensity at low intensities, consistent with the perturbative FWM mechanism, before saturating at higher intensities due to nonlinear absorption and pump depletion. Remarkably, the efficiency reaches 47% at a pump intensity of approximately 100 GW/cm², corresponding to a pump energy density of ~106 pJ/μm². To our knowledge, this represents the highest FWM conversion efficiency reported for any nanostructured device.

Figure 2b shows the calculated total intensity enhancement within the ITO layer as a function of wavelength and pump-induced plasma-frequency shift. Since the efficiency of degenerate four-wave mixing depends on the local electric fields of the interacting waves, the nonlinear conversion scales with the enhancements of the pump, signal, and idler modes^{33, 34}. The total intensity enhancement is defined as $\mathcal{F}_{\text{total}} = \langle \mathcal{F}_{\text{pump}} \rangle^2 \langle \mathcal{F}_{\text{signal}} \rangle \langle \mathcal{F}_{\text{idler}} \rangle$. The corresponding averaged intensity enhancements within the ITO layer, $\mathcal{F}_j = \langle |E_j/E_0|^2 \rangle_{\text{ITO}}$ for $j \in \{\text{pump, signal, idler}\}$, together with the total intensity enhancement relevant for FWM efficiency, are presented in Supplementary Note 5 for the high-Q sample, low-Q sample, and a bare ITO film.

To characterize the spectral dependence of the DFWM efficiency, we measured the idler generation across the ENZ spectral region from 1130 nm to 1400 nm at a fixed pump intensity of 100 GW/cm² (Fig. 2c). The High-Q sample (1549 nm spacer) exhibits peak efficiency near 1300 nm, with efficiencies exceeding 25% maintained over a broad wavelength range. The idler efficiencies as a function of pump intensity for different input laser wavelengths are shown in Supplementary Note 6. Comparison with measurements on a bare 310-nm-thick ITO film (see Supplementary Note 7) reveals that the nanostructure enhances the FWM efficiency by a factor of 2–4 throughout the ENZ region. This enhancement directly confirms the role of the Brewster mode-induced intensity enhancements in boosting the nonlinear response (see Supplementary Note 8).

We also characterized a Low-Q sample with a 101-nm SiO₂ spacer (Fig. 2d). Despite a 15-fold reduction in spacer thickness, the DFWM efficiency remains comparable to that of the High-Q sample, indicating similar total field intensity enhancement factors in both designs. The primary difference is the spectral region of maximum enhancement, demonstrating that the ENZ nanostructure can be engineered to optimize FWM efficiency at any desired wavelength within the ENZ band by adjusting the spacer thickness.

Frequency non-degenerate FWM, where $\omega_{\text{pump}} \neq \omega_{\text{signal}}$, enables wavelength conversion across different

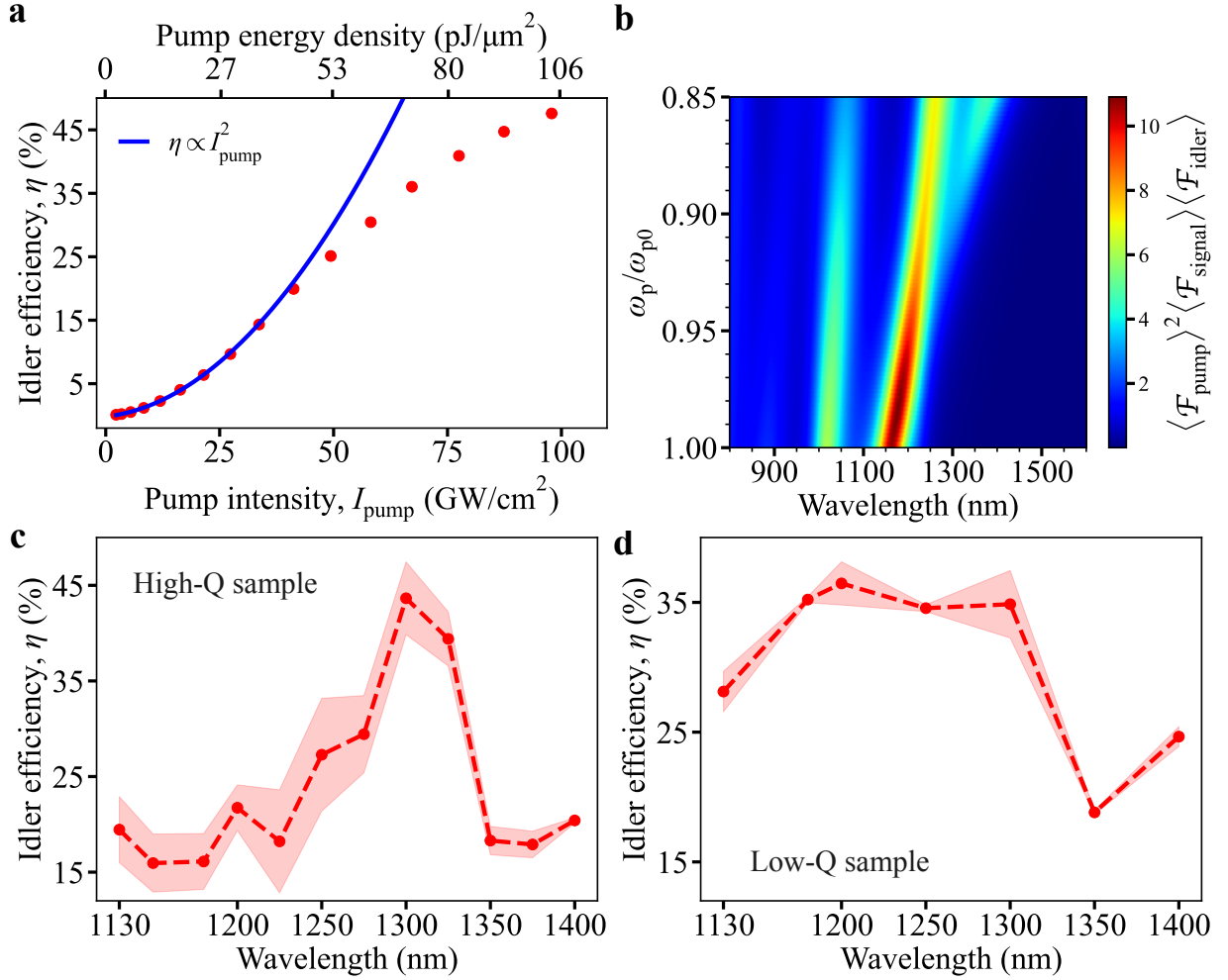


FIG. 2. **Frequency-degenerate four-wave mixing in the ENZ nanostructure.** **a**, Idler conversion efficiency versus pump intensity for 1300 nm pump-signal wavelength, showing quadratic dependence (dashed line) and saturation, with maximum efficiency of 45% at $\sim 100 \text{ GW}/\text{cm}^2$. Here, the FWM conversion efficiency is defined as the ratio of output idler power to input signal power. **b**, TMM-calculated total intensity enhancement factor as a function of wavelength and pump-induced plasma frequency shift (ω_p/ω_{p0}). The color map shows the redshift of the field enhancement within ITO as the plasma frequency changes with the pump. **c**, Idler conversion efficiency versus wavelength for the High-Q sample (1549 nm spacer) at 100 GW/cm^2 pump intensity, showing broadband enhancement across the ENZ region. **d**, Idler conversion efficiency versus wavelength for the Low-Q sample (101 nm spacer), demonstrating comparable peak efficiency with shifted spectral response.

spectral channels—a capability essential for telecommunications and quantum networking applications. To explore this regime, we fixed the pump wavelength at 1300 nm (near the peak DFWM efficiency) and varied the signal wavelength.

Figure 3a shows the spectrum of the incident pump (blue, centered at 1300 nm), incident signal (red, centered at 1275 nm), and generated idler (orange, centered at 1326 nm). The incident signal and generated idler are normalized with respect to the pump. In Supplementary Notes 9 and 10, the intensity-dependent evolution of the reflected pump, reflected signal, and the generated idler spectra for both degenerate and non-degenerate cases is shown. The reflected pump and reflected signal exhibit clear spectral redshifts with respect to pump intensity,

consistent with adiabatic frequency conversion (AFC) in ITO^{35–37}.

The non-degenerate FWM bandwidth, shown in Fig. 3b, reveals an efficiency exceeding 5% for signal wavelengths spanning 1200–1400 nm. The 3-dB bandwidth of approximately 70.54 nm around 1307.3 nm covers most of the telecommunications O-band, indicating that our nanostructure can serve as a broadband wavelength converter. From this spectral bandwidth, we estimate the material response time to be ~ 12.85 fs, consistent with the ultrafast electronic nonlinearity expected for ENZ materials. The quadratic dependence of the idler efficiency on pump intensity for different signal wavelengths, confirming the FWM origin, is shown in Supplementary Note 11.

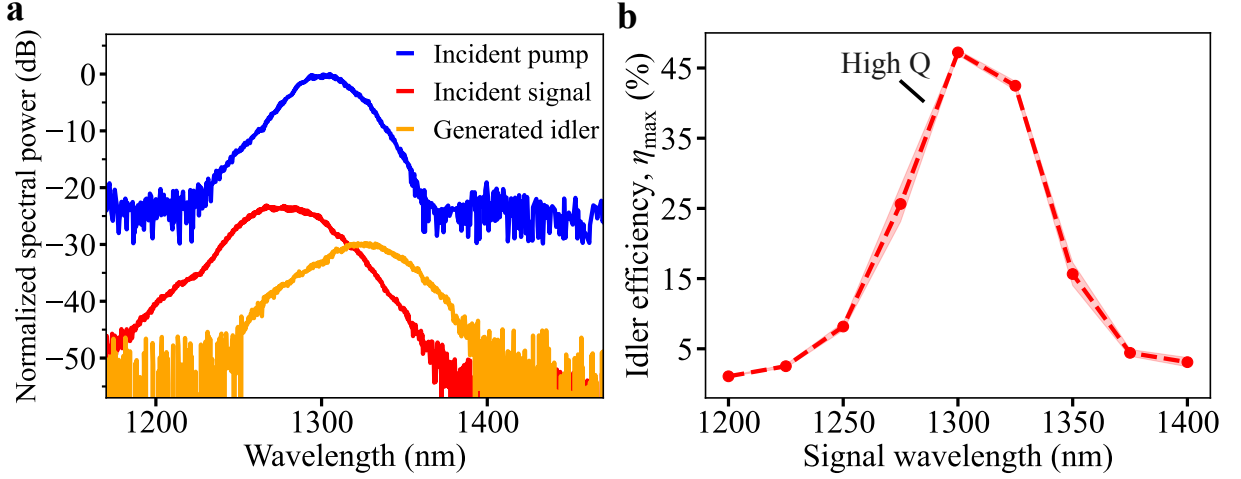


FIG. 3. **Non-degenerate four-wave mixing in the ENZ nanostructure.** **a**, Spectral characteristics showing the incident pump (blue, centered at 1300 nm) and signal (red, centered at 1275 nm) alongside the generated idler (orange, centered at 1326 nm). The incident signal and generated idler are normalized with respect to the pump. **b**, Idler efficiency as a function of signal wavelength for fixed 1300 nm pump at 100 GW/cm², revealing ~ 70 nm bandwidth covering most of the telecommunications O-band. The peak efficiency occurs at the degenerate condition (1300 nm) and decreases as the signal wavelength deviates from the pump.

For a frequency-degenerate pump-signal configuration, in addition to enhanced four-wave mixing, the strong nonlinear response of the ENZ nanostructure enables high-order wave-mixing processes, including six-wave mixing (6WM), eight-wave mixing (8WM), ten-wave mixing (10WM), and twelve-wave mixing (12WM). These processes can be understood within a self-diffraction framework, where the interference of the pump and signal beams creates an effective nonlinear grating in the material. In this picture, a pump beam with wavevector k_{pump} and a signal beam with wavevector k_{signal} interact to generate wave-mixing components corresponding to different diffraction orders. The standard four-wave mixing process corresponds to the wavevector relation $2k_{\text{pump}} - k_{\text{signal}}$. Higher-order processes arise naturally from the same nonlinear interaction, with six-wave mixing corresponding to $3k_{\text{pump}} - 2k_{\text{signal}}$, and, more generally, higher-order mixing processes following the form $(n+1)k_{\text{pump}} - nk_{\text{signal}}$ for the dominant branch. The asymmetry in the diffraction orders stems from the intensity difference between the pump and signal beams. For equal pump and signal intensities, the diffraction orders are symmetric about the pump and signal reflected beams. Energy conservation requires the corresponding frequencies to satisfy $(n+1)\omega_{\text{pump}} - n\omega_{\text{signal}}$. For the frequency-degenerate case considered here, $\omega_{\text{pump}} = \omega_{\text{signal}}$, and therefore all generated orders remain at the same optical frequency and are distinguished by their wavevectors. Schematically, the high-order wave-mixing process for a strong pump and a weak signal is illustrated in Figure 4a (see Supplementary Note 12 for high-resolution infrared camera images).

Figure 4b shows the spectrum of the idler correspond-

ing to eight-, six-, and four-wave mixing, along with the reflected pump and signal spectra when the pump and signal are both set at 1300 nm. The spectra were collected for a pump intensity of 100 GW/cm² and a signal intensity of 12 GW/cm². For visual purposes, all spectra except the pump are multiplied by a factor of 50. Near-infrared images of all the diffraction orders observed for both the ENZ-nanostructure and monolithic ITO, along with the maximum six-wave mixing efficiency of 10% and eight-wave mixing efficiency of 2%, and their dependence on pump and signal intensities, are provided in the Supplementary Note 12. To our knowledge, these efficiencies are the highest reported thus far for any nanostructures.

DISCUSSION

The $47.2 \pm 0.4\%$ FWM conversion efficiency demonstrated in our ENZ nanostructure represents a transformative advancement for nanostructured nonlinear optical devices. We compare our results with those of other FWM platforms in Supplementary Note 13. Our efficiency exceeds that of previous ENZ thin films by 3-4 times and surpasses plasmonic and metasurface approaches by orders of magnitude. Remarkably, our sub-wavelength nanostructure achieves conversion efficiencies comparable to silicon photonic waveguides that are three orders of magnitude longer (millimeters to centimeters versus $\sim 2 \mu\text{m}$).

Several factors contribute to this exceptional performance. First, the ENZ condition in ITO provides an intrinsically large $\chi^{(3)}$ nonlinearity arising from hot-electron dynamics and the field enhancement associated with the near-zero permittivity^{26, 28, 29}. Second, the

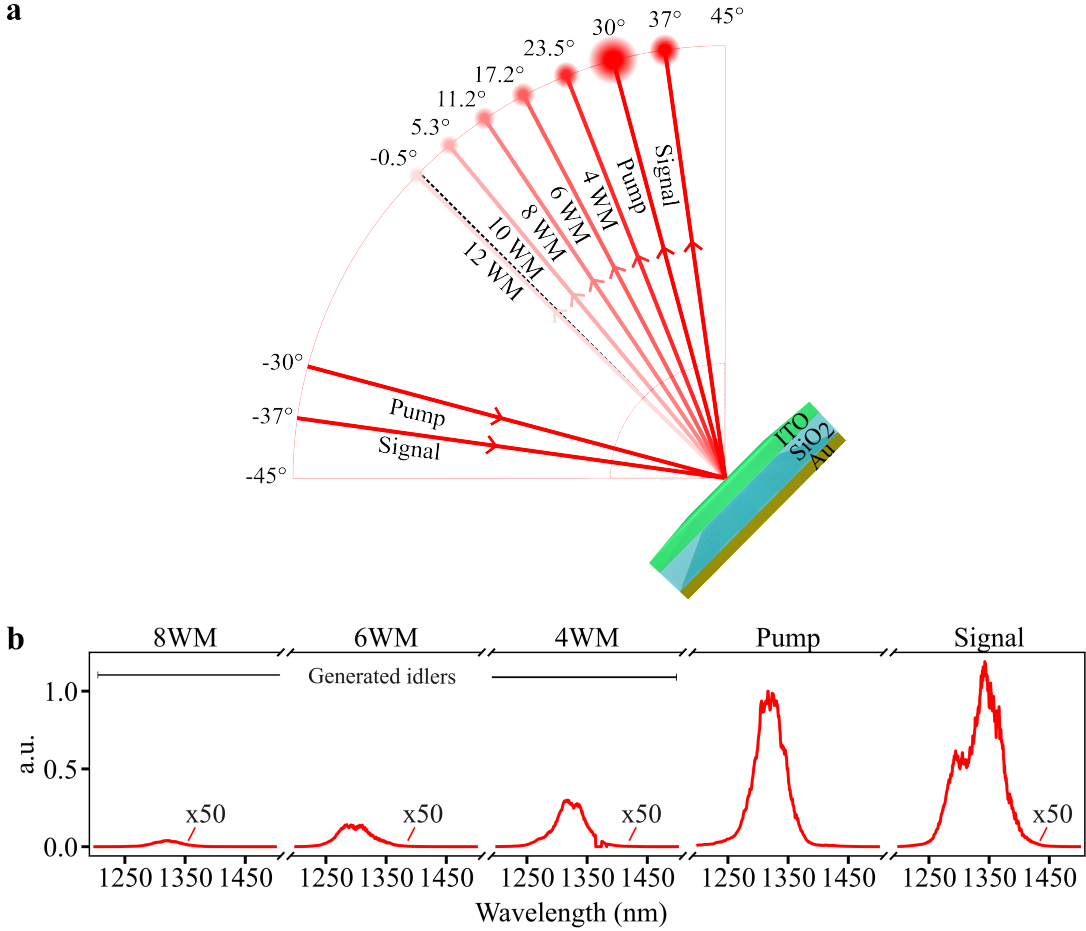


FIG. 4. High-order wave mixing in an ENZ nanostructure. **a**, Schematic illustration of nonlinear wave mixing, showing the generation of multiple idlers corresponding to higher-order wave-mixing processes. The observed idlers extend up to 12WM. **b**, Measured output spectra showing idlers generated through four-wave mixing (4WM), six-wave mixing (6WM), and eight-wave mixing (8WM), together with the reflected pump and reflected signal, under frequency-degenerate excitation at 1300 nm. The pump and signal intensities are 100 GW/cm² and 12 GW/cm², respectively. The generated idler spectra and reflected signal spectra are multiplied by 50 for clarity.

Gires-Tournois etalon geometry concentrates the optical field within the ITO layer, multiplicatively enhancing the effective nonlinear response. Third, the sub-wavelength thickness naturally relaxes phase-matching constraints, enabling efficient FWM without the careful dispersion engineering required in long waveguides. Fourth, the ITO top layer serves as a protective barrier for the underlying Au mirror, enabling operation at higher pump intensities than would be possible with exposed plasmonic structures.

The dynamic tuning observed under intense pumping—where the pump-induced refractive index change shifts the resonance—provides an additional mechanism that can be engineered for specific applications. This effect enables wavelength-dependent optimization of the field enhancement and could potentially be exploited for time-varying photonic functionalities³⁸.

Our results have immediate implications for several ap-

plication areas. For integrated photonics, the demonstrated efficiencies and broad bandwidth position ENZ nanocavities as compact wavelength converters operating across the telecommunications O-band. By adjusting the ITO composition or using alternative ENZ materials, such as aluminum-doped zinc oxide (AZO), the operating wavelength can be readily shifted to the C-band³⁹. For real-time holography applications, the nanoscale interaction length avoids the image degradation associated with extended waveguide geometries, while the high efficiency provides adequate signal strength for practical implementations⁴⁰.

Perhaps most significantly, our results suggest a pathway toward efficient spontaneous FWM (SFWM) for quantum photon-pair generation. Current SFWM demonstrations in subwavelength nonlinear films have been limited by weak nonlinearities⁴¹. The unity-order stimulated FWM efficiency demonstrated here, combined with the relaxed phase-matching that enables broadband

photon-pair generation, indicates that ENZ nanocavities could overcome these limitations. Theoretical predictions suggest that field-enhancement factors achievable in optimized structures could push SFWM rates to practically useful levels³³.

Further efficiency improvements are possible through integration with dielectric or plasmonic metasurfaces to provide additional resonant enhancement, optimizing ITO deposition conditions to minimize losses while maintaining the ENZ response, and exploring alternative geometries to maximize the spatial overlap between the etalon mode and the ENZ region.

In conclusion, we have demonstrated that ENZ-based Gires-Tournois nanostructures achieve unity-order FWM conversion efficiency in a simple, sub-wavelength-thick, easily fabricated structure. The 47% efficiency and 70 nm bandwidth represent new benchmarks for nanostructured nonlinear optical platforms, establishing ENZ nanocavities as a transformative technology for integrated nonlinear photonics and quantum optical applications.

MATERIALS AND METHODS

Sample fabrication

The ENZ nanostructure samples were fabricated by sequential thin-film deposition on glass substrates. A 333-nm-thick ITO film, which acts as the front partial mirror and nonlinear active layer, was deposited similarly to the protocol described in⁴², followed by an SiO₂ spacer layer of either 1549 nm (High-Q) or 101 nm (Low-Q) thickness and a 200-nm-thick Au layer, which acts as the back reflector. Film thicknesses and optical constants were characterized by spectroscopic ellipsometry. The optical permittivity of the ITO films was extracted from ellipsometry measurements and fitted with a Drude model to determine the ENZ wavelength.

Optical characterization

Linear reflectance spectra were measured using a white-light source with angle-resolved detection for TM-polarized light. Four-wave mixing experiments employed ~100 fs pulses generated by two optical parametric amplifiers pumped by a Ti:sapphire regenerative amplifier (800 nm, 1 kHz repetition rate). For DFWM measurements, a single OPA output was split to generate pump and signal beams, whereas two independently tunable OPAs were used for non-degenerate FWM. Beam powers

and spectra were measured using calibrated germanium photodetectors and an optical spectrum analyzer, respectively. Additional details of the nonlinear optical setup are provided in Supplementary Note 3.

Transfer matrix method simulations

Reflectance spectra and field distributions were calculated using the transfer matrix method with measured optical constants for each layer. Pump-induced changes were modeled by varying the plasma frequency of the ITO Drude model. Additional details of the TMM calculations are provided in Supplementary Note 1.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGEMENTS

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AUTHOR CONTRIBUTIONS

M.Z.A. and R.A. conceptualized the experiment and designed the sample. Y.V., T.L., and M.Z.A. initiated the experimental work. Y.V. and T.L. performed all measurements, analyzed the data, and developed numerical models, assisted by J.U. and M.Z.A. S.V. and J.R.H. fabricated the samples. Y.M. and R.M.C.C. built the linear measurement setup. Y.V. and T.L. wrote the initial draft. All authors discussed results and contributed to manuscript preparation. J.U., M.Z.A., and R.W.B. supervised the project.

CONFLICT OF INTEREST

The authors declare no competing interests.

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Supporting Information: Unity-Order Wave Mixing in Epsilon-Near-Zero Nanostructures

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SUPPLEMENTAL NOTE 1: TRANSFER MATRIX METHOD CALCULATIONS FOR THE ENZ NANOSTRUCTURES

To calculate the theoretical reflectance spectra of the ENZ nanostructure, we employed a Python-based Transfer Matrix Method (TMM) as described in Ref. [1]. The substrate is treated incoherently in all cases to avoid thin-film Fabry-Perot fringes. As shown in Fig. S1, we calculated the reflectance for various angles of incidence for three cases: (a) a monolithic ITO film and ENZ nanostructures with spacer thicknesses of (b) 101 nm (Low-Q sample) and (c) 1549 nm (High-Q sample). For the nanostructure simulations, the structure consists of four layers: an incoherently treated silicon substrate (2 mm), an ITO film (333 nm), a silicon spacer (101 nm or 1549 nm), and a gold layer (200 nm). All linear optical parameters were experimentally obtained from ellipsometry.

Furthermore, we have also calculated the electric field distributions for all three cases (ITO thin film and ENZ nanostructures with spacer thicknesses of 101 nm and 1549 nm). Figure S2 shows the intensity distributions as a function of wavelength and device position at two angles (30° and 37°), corresponding to the pump and signal angles in the FWM experiments.

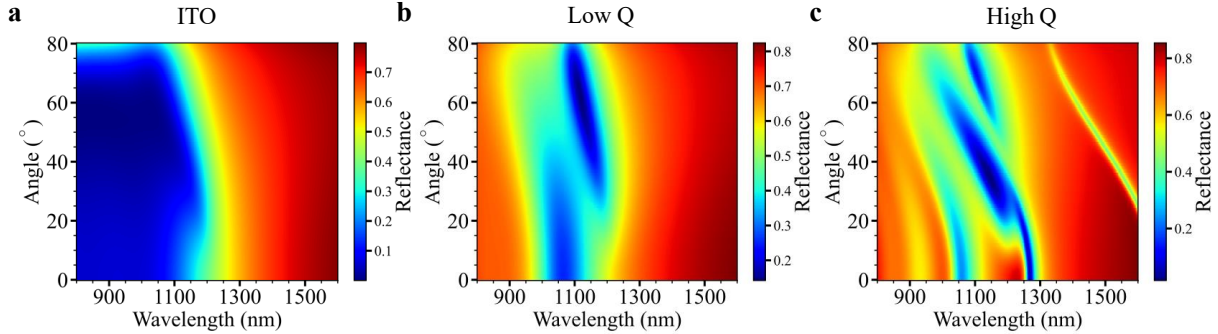


FIG. S1. **The linear reflectance calculations using TMM.** The theoretical linear reflectance spectra as functions of incidence angles and wavelengths for monolithic (a) ITO film, and the ENZ nanostructures with the spacer thickness of (b) 101 nm and (c) 1549 nm.

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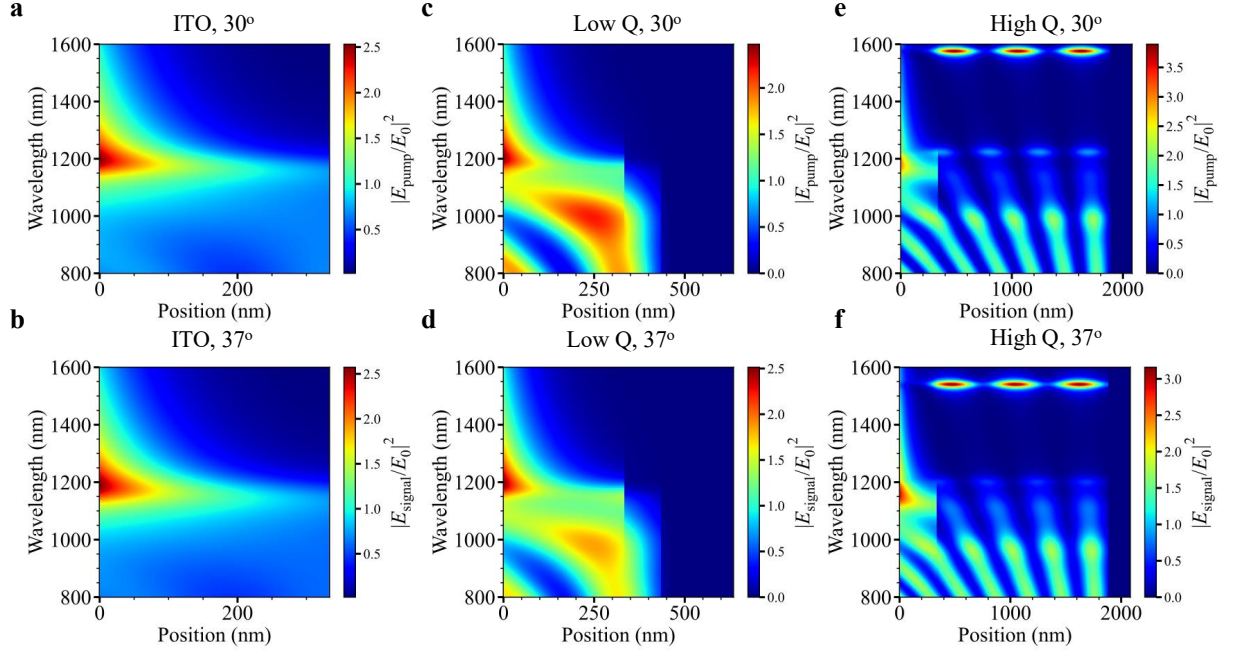


FIG. S2. **The electric field distributions for the ENZ nanostructures.** The intensity distribution as a function of wavelength and device position for the three investigated cases: monolithic ITO film (a) pump and (b) signal configurations; ENZ nanostructure with 101 nm spacer for (c) pump and (d) signal configurations; and ENZ nanostructure with 1549 nm spacer for (e) pump and (f) signal configurations.

SUPPLEMENTAL NOTE 2: LINEAR REFLECTANCE MEASUREMENTS FOR ENZ NANOSTRUCTURES

We performed a series of linear measurements using a continuous white-light source with wavelengths ranging from 800 nm to 1600 nm and various angles of incidence (10° to 60°) on two different ENZ nanostructures (spacer thicknesses of 1549 nm and 101 nm). The reflectance of these two samples is shown in Fig. S3a and Fig. S3b.

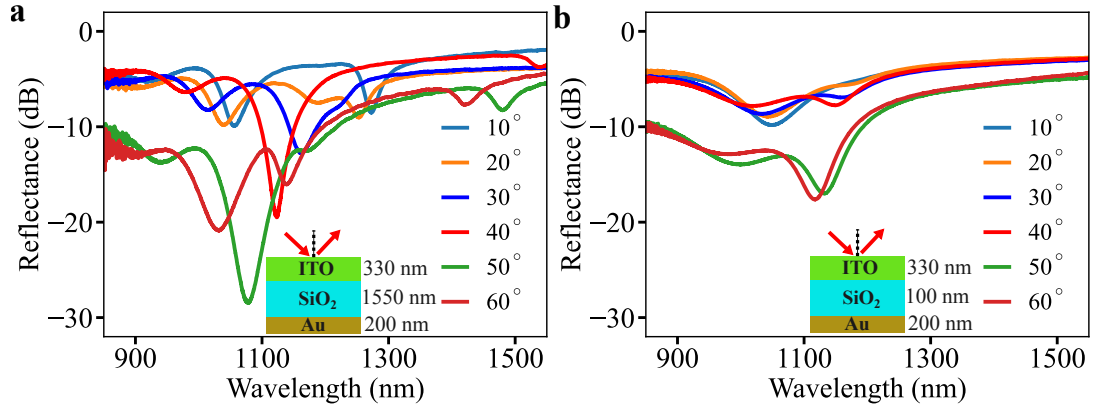


FIG. S3. **The linear reflectance measurements for the ENZ nanostructure samples.** The linear reflectance spectra for ENZ nanostructure samples with the spacer thickness of (a) 1549 nm and (b) 101 nm. Both sets of linear measurements are conducted with various angles of incidence from 10° to 60° .

Figure S4 shows the comparison between the experimental and TMM-based linear measurements for the ENZ nanostructure with a spacer thickness of 1549 nm. All material optical parameters are obtained using ellipsometry.

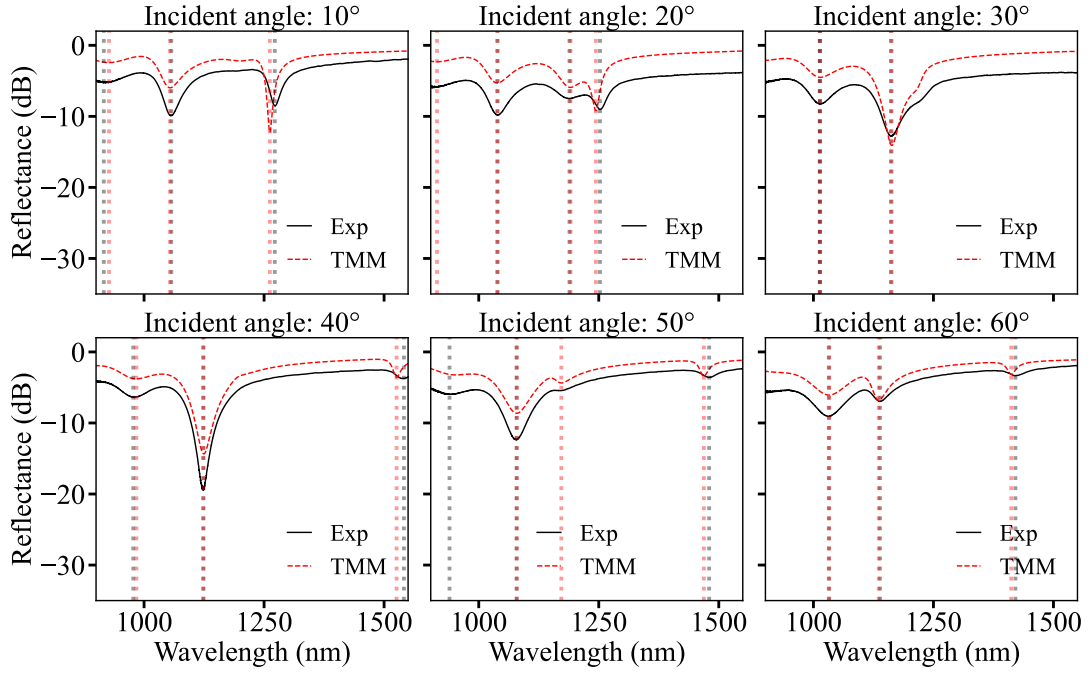


FIG. S4. **The linear reflectance of the ENZ nanostructure sample.** Comparison of experimental and TMM-based linear reflectance spectra for the ENZ nanostructure sample with the spacer thickness of 1549 nm for various angles of incidence from 10° to 60° .

SUPPLEMENTAL NOTE 3: EXPERIMENTAL SETUP FOR FWM MEASUREMENTS

We conducted a series of pump-signal experiments on the ENZ nanostructure to observe FWM generation. A Ti:Sapphire laser generated ~ 100 fs laser pulses, and its wavelength was tuned using two optical parametric amplifiers (TOPAS Prime, Spectra Physics), which are labeled as OPA1 and OPA2. The output beams from OPA1 and OPA2 serve as the signal and pump beams, respectively. We then independently tuned the intensities of both beams using a pair of half-wave plates mounted on rotational stages and Glan-Taylor polarizers. Both pulses are set to be p-polarized. The signal beam line features a translational stage (DDSM100, Thorlabs) that controls the delay time ($\Delta\tau$) between the pump and signal beams. The beam sizes of the pump and signal were adjusted to $63\ \mu\text{m}$ using plano-convex lenses. The signal intensity was maintained at approximately $1.5\ \text{GW}/\text{cm}^2$ to prevent signal-induced optical nonlinearities, while the pump intensity varied from 1 to $100\ \text{GW}/\text{cm}^2$. The pump beam is incident at 30° and the signal beam at 37° on the sample, allowing the beams to interact with the ENZ nanostructure's modes, thereby maximizing FWM generation efficiency. The FWM signal is generated at an incident angle of 23° to the sample and measured using calibrated germanium photodetectors (PH20-Ge-OD2-D0, Gentec-eo). Spectra were recorded with an optical spectrum analyzer. Data acquisition was automated using custom Python software. Figure S5 illustrates the schematic of the experimental setup.

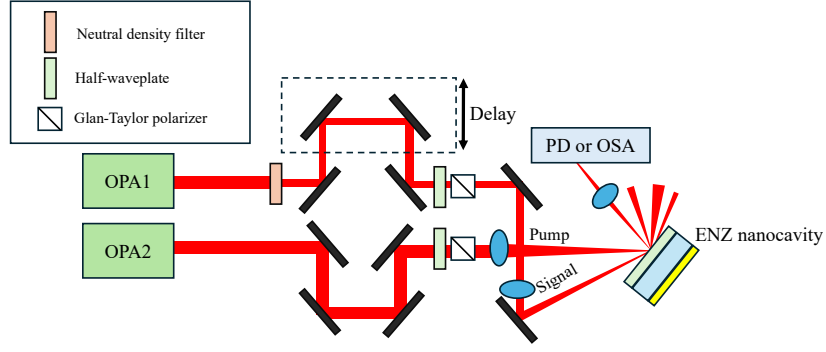


FIG. S5. **The schematic of the experimental setup.** BS: pellicle beamsplitter. OPA: optical parametric amplifiers. OSA: optical spectrum analyzer. PD: photodetector.

SUPPLEMENTAL NOTE 4: NONLINEAR TMM REFLECTANCE FOR ENZ NANOSTRUCTURES

The large changes in refractive index of ITO, Δn_{ITO} , under strong optical pumping change the optical path length of all the nanostructures [2–4], leading to frequency shifting of both the Brewster mode and the etalon mode. To simulate the frequency shifting of the nanostructure, we performed TMM calculations by reducing the plasma frequency of ITO for pump, signal, and idler configurations in ENZ nanostructures with spacer thickness of 1549 nm (Fig. S6) and 101 nm (Fig. S7). Here, $\omega_p/\omega_{p0} = 1$ corresponds to the unpumped linear case, while $\omega_p/\omega_{p0} = 0.85$ is used to approximate the optically pumped state of ITO, resulting in a refractive-index change of $\Delta n_{ITO} \approx 0.7$ at the ENZ wavelength. In all cases, the modes are redshifted to 1300 nm.

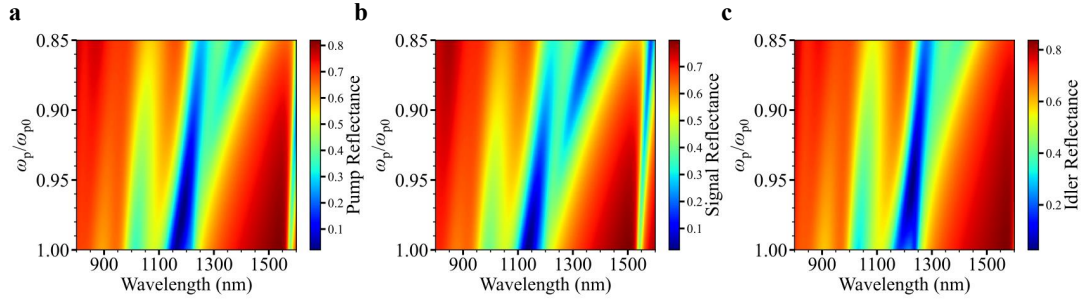


FIG. S6. **ENZ nanostructure mode redshifting simulations using TMM with spacer thickness of 1549 nm.** The TMM-simulated reflectance of the ENZ nanostructure as functions of changes in plasma frequency (ω_p/ω_{p0}) and wavelength (nm) for (a) pump, (b) signal, and (c) idler.

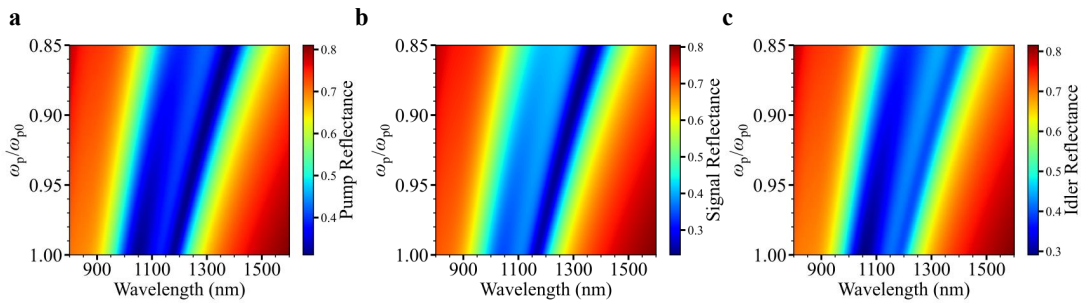


FIG. S7. **ENZ nanostructure mode redshifting simulations using TMM with spacer thickness of 101 nm.** The TMM-simulated reflectance of the ENZ nanostructure as functions of changes in plasma frequency (ω_p/ω_{p0}) and wavelength (nm) for (a) pump, (b) signal, and (c) idler.

SUPPLEMENTAL NOTE 5: INTENSITY ENHANCEMENTS FOR PUMP, SIGNAL, AND IDLER BEAMS FOR ENZ NANOSTRUCTURES

We performed a set of intensity-enhancement calculations using TMM for the pump, signal, and idler beams for spacer thicknesses of 1549 nm and 101 nm. The corresponding averaged intensity enhancement factors within the ITO layer are defined as

$$\mathcal{F}_j = \left\langle \left| \frac{E_j}{E_0} \right|^2 \right\rangle_{\text{ITO}}, \quad j \in \{\text{pump, signal, idler}\}, \quad (1)$$

where the averaging is performed over the ITO thickness. The total intensity enhancement factor, $\mathcal{F}_{\text{total}}$, is calculated as

$$\mathcal{F}_{\text{total}} = \langle \mathcal{F}_{\text{pump}} \rangle^2 \langle \mathcal{F}_{\text{signal}} \rangle \langle \mathcal{F}_{\text{idler}} \rangle. \quad (2)$$

TMM calculations for samples with spacer thicknesses of 1549 nm and 101 nm are shown in Figs. S8 and S9, respectively. For reference, we also performed the same calculations for a monolithic ITO film (Fig. S10). At 1300 nm and for the plasma frequency corresponding to the optically pumped state of ITO ($\omega_p/\omega_{p0} = 0.85$), the total field enhancement, $\mathcal{F}_{\text{total}}$, of the ENZ nanostructure with a spacer thickness of 1549 nm is 4.27, whereas the corresponding value for the monolithic ITO film is 0.79. Thus, the ENZ nanostructure provides a 5.4-fold enhancement in $\mathcal{F}_{\text{total}}$ compared to ITO at 1300 nm.

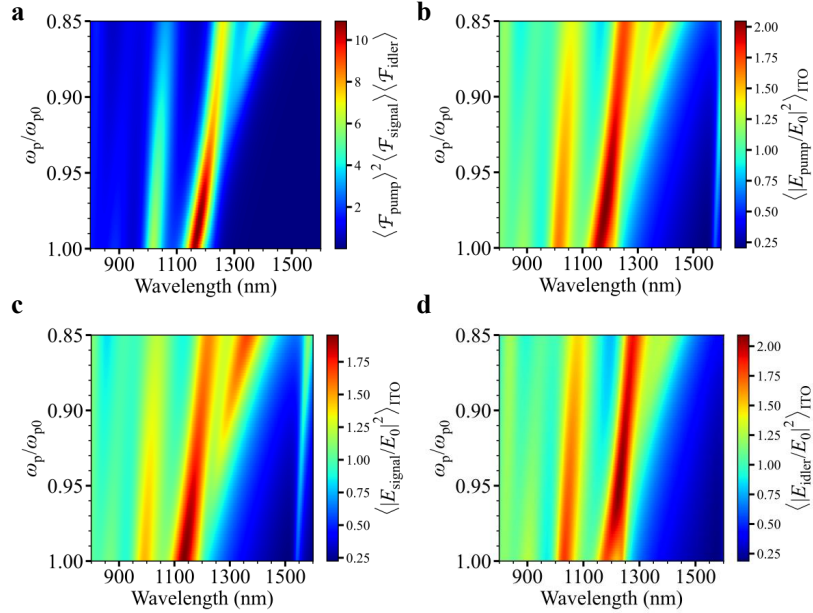


FIG. S8. **Intensity enhancements calculations using TMM for the ENZ nanostructure sample with spacer thickness of 1549 nm.** The intensity enhancements (IE) as functions of changes in plasma frequency (ω_p/ω_{p0}) and wavelength (nm) for (a) total, (b) signal, (c) pump, and (d) idler.

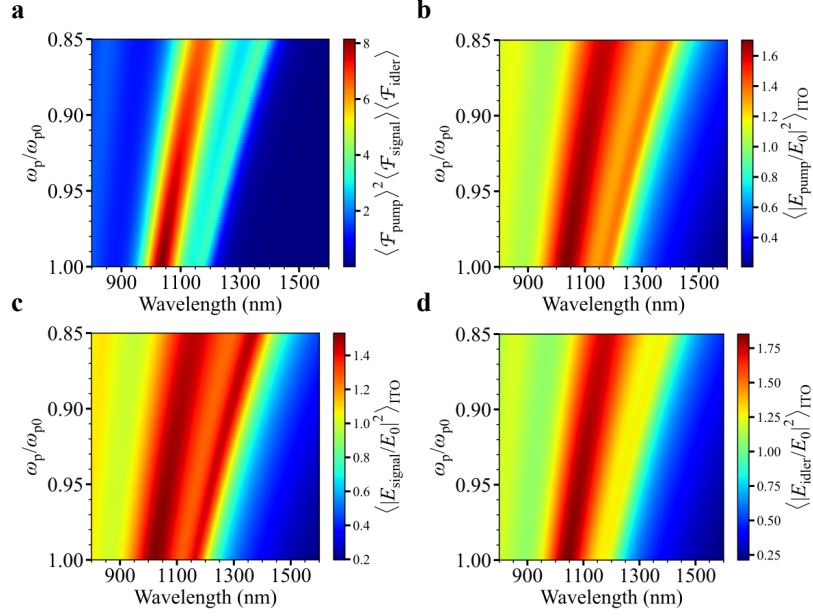


FIG. S9. **Intensity enhancements calculations using TMM for the ENZ nanostructure sample with spacer thickness of 101 nm.** The intensity enhancements (IE) as functions of changes in plasma frequency (ω_p/ω_{p0}) and wavelength (nm) for (a) total, (b) signal, (c) pump, and (d) idler.

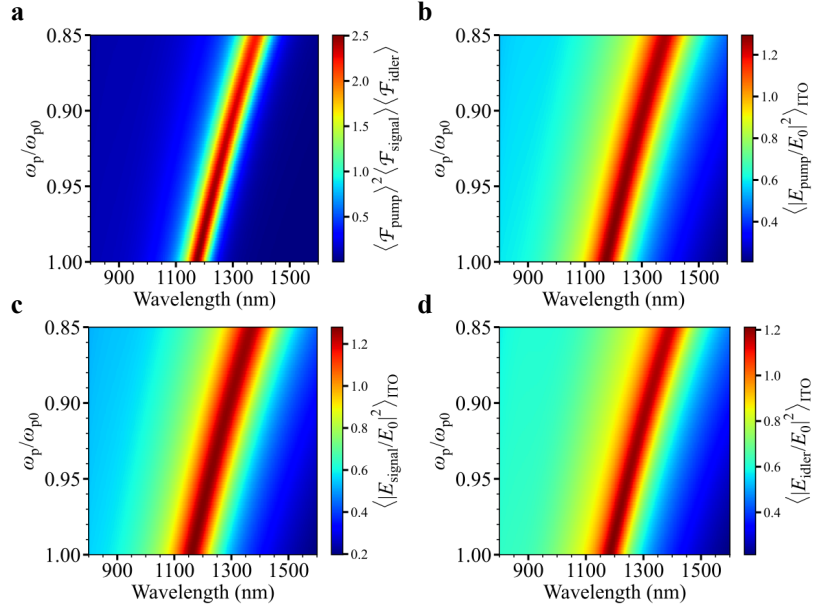


FIG. S10. **Intensity enhancements calculations using TMM for ITO film.** The intensity enhancements (IE) as functions of changes in plasma frequency (ω_p/ω_{p0}) and wavelength (nm) for (a) total, (b) signal, (c) pump, and (d) idler.

SUPPLEMENTAL NOTE 6: INTENSITY-DEPENDENCE ON FWM GENERATION FOR THE ENZ NANOSTRUCTURE

We measured the idler efficiencies of the ENZ-nanostructure with a spacer thickness of 1549 nm as a function of pump intensity (GW/cm^2) for various input laser wavelengths (Fig. S11). A quadratic fit was applied to each case, with the results and fitting parameters presented in the sub-figure legends. The wavelengths of the pump and signal are mentioned in the title of each sub-figure.

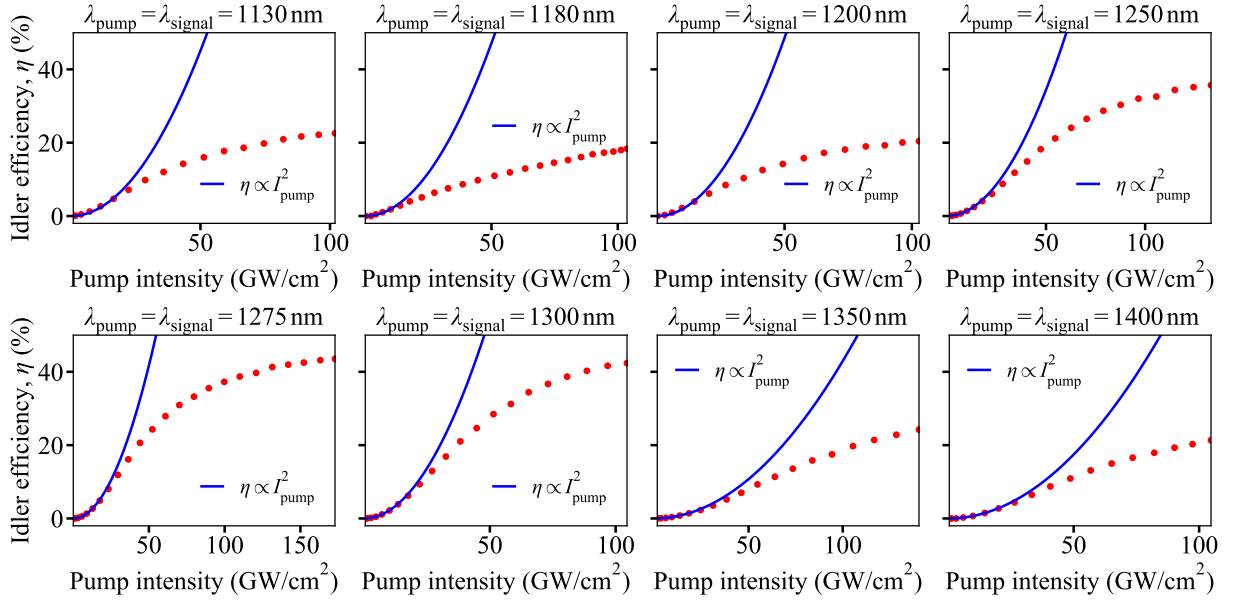


FIG. S11. **The intensity dependence for DFWM efficiencies with different wavelengths.** The idler efficiencies as a function of pump intensity with the laser wavelengths of 1130 nm, 1180 nm, 1200 nm, 1250 nm, 1275 nm, 1300 nm, 1350 nm, and 1400 nm.

SUPPLEMENTAL NOTE 7: DFWM MEASUREMENTS FOR MONOLITHIC ITO FILM

To determine the FWM enhancements due to the ENZ nanostructure, we performed the same set of pump-signal experiments for a monolithic ITO thin film with a thickness of 310 nm. We simultaneously measure the reflected and transmitted idler efficiencies at input wavelengths from 1130 to 1400 nm. The idler efficiencies are shown in Fig. S12.

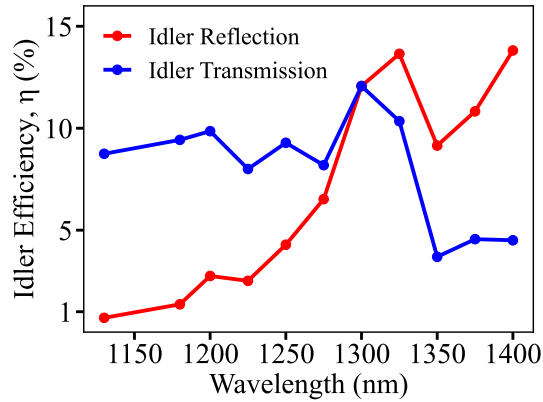


FIG. S12. **The idler efficiencies for monolithic ITO thin film.** The reflected (red) and transmitted (blue) idler efficiencies for a monolithic ITO film with a thickness of 310 nm.

SUPPLEMENTAL NOTE 8: NONLINEAR COUPLED-MODE EQUATIONS FOR FWM CONVERSION EFFICIENCY

FWM conversion efficiency in an ENZ film (ITO)

We begin from the nonlinear wave equation in a source-free, nonmagnetic medium,

$$\nabla^2 \tilde{E}_n - \frac{\epsilon_n}{c^2} \frac{\partial^2 \tilde{E}_n}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \tilde{P}_n^{NL}}{\partial t^2}. \quad (3)$$

Here, the subscript n denotes the frequency component under consideration. For four-wave mixing (FWM), the relevant frequencies are the pump, signal, and idler frequencies, denoted by p , s , and i , respectively. The electric field at each frequency is written as

$$\tilde{E}_n(z, t) = A_n(z) e^{i(k_n z - \omega_n t)} + \text{c.c.}, \quad (4)$$

where $A_n(z)$ is the slowly varying complex field amplitude and k_n is the wavevector,

$$k_n = \frac{n_n \omega_n}{c}, \quad (5)$$

with refractive index defined as $n_n^2 = \epsilon_n$.

The nonlinear polarization at the idler frequency is written as

$$\tilde{P}_i^{NL}(z, t) = P_i^{NL}(z) e^{-i\omega_i t} + \text{c.c.} \quad (6)$$

For the degenerate FWM process,

$$\omega_i = 2\omega_p - \omega_s, \quad (7)$$

the nonlinear polarization amplitude becomes

$$P_i^{NL}(z) = 3\epsilon_0 \chi^{(3)} A_p^2(z) A_s^*(z) e^{i(2k_p - k_s)z}. \quad (8)$$

Substituting this expression into the nonlinear wave equation and applying the slowly varying envelope approximation yields

$$\frac{dA_i}{dz} = i \frac{3\chi^{(3)}\omega_i}{2n_i c} A_p^2 A_s^* e^{i\Delta k z}, \quad (9)$$

where the phase mismatch is

$$\Delta k = 2k_p - k_s - k_i. \quad (10)$$

Under the undepleted pump-signal approximation, we retain only the coupled-mode equation for the idler.

The pump beam is incident at 30° and the signal beam at 37° with respect to the surface normal. The generated idler is collected near 23° , as determined by transverse momentum conservation,

$$\sin \theta_i = 2 \sin \theta_p - \sin \theta_s. \quad (11)$$

Substituting the experimental angles gives

$$\sin \theta_i = 2 \sin(30^\circ) - \sin(37^\circ), \quad (12)$$

which yields

$$\theta_i \approx 23.5^\circ. \quad (13)$$

Thus, the idler is collected close to the phase-matched direction, and the efficiency calculation is performed under the approximation $\Delta k \approx 0$.

Integrating the idler equation over the nonlinear interaction length L gives

$$A_i(L) = i \frac{3\chi^{(3)}\omega_i}{2n_i c} A_p^2 A_s^* L. \quad (14)$$

The time-averaged optical intensity is related to the field amplitude by

$$I_n = 2n_n \epsilon_0 c |A_n|^2. \quad (15)$$

Using this relation, the generated idler intensity becomes

$$I_i = \frac{9(\omega_i \chi^{(3)})^2}{4n_i n_s n_p^2 c^4 \epsilon_0^2} I_p^2 I_s L^2. \quad (16)$$

The FWM conversion efficiency is defined as

$$\eta = \frac{I_i}{I_s}. \quad (17)$$

Therefore, for an ITO film, the FWM conversion efficiency, assuming negligible linear absorption over the nonlinear interaction length, is defined as

$$\boxed{\eta_{\text{ITO}} = \frac{9(\omega_i \chi^{(3)})^2}{4n_i n_s n_p^2 c^4 \epsilon_0^2} I_p^2 L^2.} \quad (18)$$

This expression is consistent with the treatment of FWM in ENZ films reported by Vezzoli *et al.* [5, 6], where the nonlinear conversion efficiency was shown to scale strongly near the ENZ wavelength due to the reduced refractive index.

In practice, absorption within the ITO layer reduces the effective interaction length available for four-wave mixing. The simplest way to account for linear absorption analytically is through an effective interaction length,

$$L_{\text{eff}} = \frac{1 - e^{-\alpha L}}{\alpha}, \quad (19)$$

where α is the linear absorption coefficient,

$$\alpha = \frac{4\pi\kappa}{\lambda}, \quad (20)$$

and κ is the imaginary part of the refractive index.

While this effective-length approach captures the dominant effect of absorption, it does not account for Fresnel transmission, reflection, or thin-film interference. In this work, these effects are incorporated through TMM calculations of the electromagnetic fields within the nonlinear layer. We define the intensity enhancement factors as

$$\mathcal{F}_j = \left\langle \left| \frac{E_j}{E_{j,\text{inc}}} \right|^2 \right\rangle_{\text{ITO}}, \quad j \in \{\text{pump, signal, idler}\}, \quad (21)$$

where the averaging is performed over the ITO thickness.

Since the nonlinear polarization responsible for idler generation scales as

$$P_i^{NL} \propto E_p^2 E_s^*, \quad (22)$$

the corresponding intensity enhancement factor governing the FWM efficiency is

$$\mathcal{F}_{\text{total}} = \langle \mathcal{F}_{\text{pump}} \rangle^2 \langle \mathcal{F}_{\text{signal}} \rangle \langle \mathcal{F}_{\text{idler}} \rangle. \quad (23)$$

For the ITO film, the FWM conversion efficiency is therefore approximated as

$$\eta_{\text{ITO}} \approx \mathcal{F}_{\text{total,ITO}} \frac{9(\omega_i \chi^{(3)})^2}{4n_i n_s n_p^2 c^4 \epsilon_0^2} I_p^2 L^2. \quad (24)$$

FWM efficiency in an ENZ nanostructure

For the ENZ nanostructure, the same formalism is applied. The intensity enhancement factors inside the ITO layer are obtained from TMM calculations, yielding the corresponding enhancement factor $\mathcal{F}_{\text{total,nanostructure}}$.

The FWM conversion efficiency is therefore

$$\eta_{\text{nanostructure}} \approx \mathcal{F}_{\text{total,nanostructure}} \frac{9(\omega_i \chi^{(3)})^2}{4n_i n_s n_p^2 c^4 \epsilon_0^2} I_p^2 L^2. \quad (25)$$

This form is analogous to cavity-enhanced FWM expressions reported for ring resonators and Fabry–Pérot nonlinear cavities, where the conversion efficiency scales with the enhancement factors at the pump, signal, and idler frequencies [7–9].

Comparison of ENZ nanostructure with ITO film

Assuming that the nonlinear susceptibility $\chi^{(3)}$, pump intensity, interaction length, and collection geometry remain unchanged between the ITO film and the ENZ nanostructure, the enhancement in FWM efficiency is primarily determined by the intensity enhancement factors within the ITO layer. At 1300 nm and for the plasma frequency corresponding to the optically pumped state of ITO ($\omega_p/\omega_{p0} = 0.85$), the total field enhancement, $\mathcal{F}_{\text{total,nanostructure}}$, of the ENZ nanostructure with a spacer thickness of 1549 nm is 4.27, whereas the corresponding value for the monolithic ITO film is 0.79. Thus, the ENZ nanostructure provides a 5.4-fold enhancement in $\mathcal{F}_{\text{total}}$ compared to ITO at 1300 nm.

$$\mathcal{F}_{\text{total,ITO}} \approx 0.79, \quad (26)$$

whereas for the ITO–SiO₂–Au nanostructure,

$$\mathcal{F}_{\text{total,nanostructure}} \approx 4.27. \quad (27)$$

The relative enhancement in FWM efficiency is therefore

$$\frac{\eta_{\text{nanostructure}}}{\eta_{\text{ITO}}} = \frac{\mathcal{F}_{\text{total,nanostructure}}}{\mathcal{F}_{\text{total,ITO}}} = 5.4. \quad (28)$$

Thus, the ITO–SiO₂–Au nanostructure is expected to provide an approximately 5.4-fold enhancement in reflected FWM efficiency relative to the monolithic ITO film.

SUPPLEMENTAL NOTE 9: FREQUENCY SHIFTING FOR THE MODES FOR DFWM

For the ENZ nanostructure with a spacer thickness of 1549 nms, we measured the reflected pump, reflected signal, and idler spectra at various pump intensities (10 to 100 GW/cm²) for the case where the input pump and signal wavelengths are 1180 nm (Fig. S13) and 1300 nm (Fig. S14). For both cases, we observed redshifts of the signal modes as the pump intensity increased. For the 1300 nm case, we also observe redshifting of the idler beams.

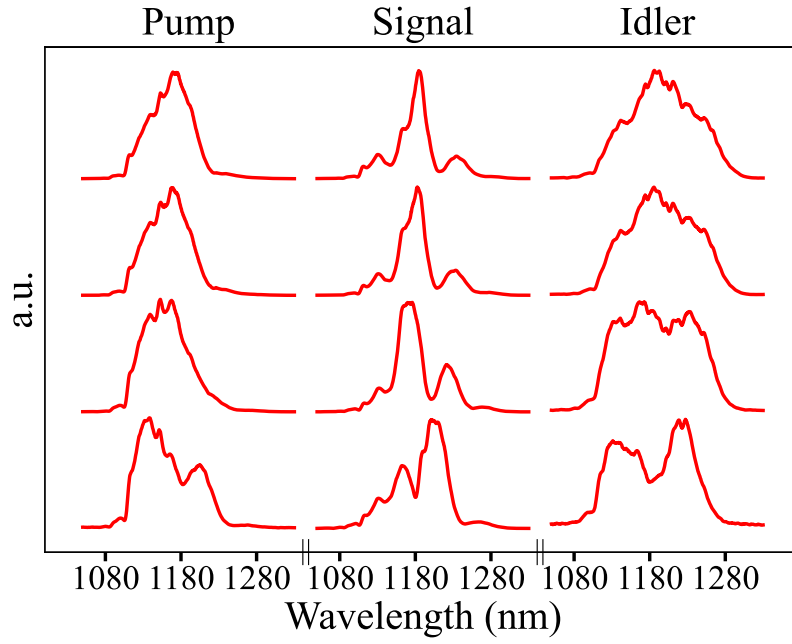


FIG. S13. **The measured spectrum with input laser wavelength of 1180 nm.** The reflected pump, reflected signal, and idler spectrum with the pump intensity from 10 to 100 GW/cm^2 for a laser wavelength of 1180 nm.

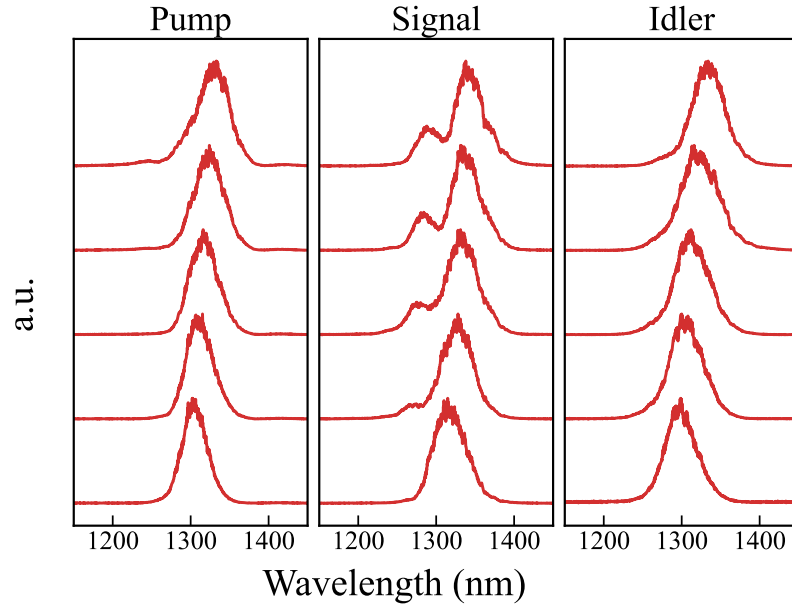


FIG. S14. **The measured spectrum with input laser wavelength of 1300 nm.** The reflected pump, reflected signal, and idler spectra with the pump intensity from 10 to 100 GW/cm^2 for a laser wavelength of 1300 nm.

SUPPLEMENTAL NOTE 10: FREQUENCY SHIFTING FOR THE MODES FOR NON-DFWM

We measured the reflected pump, reflected signal, and idler spectra at various pump intensities for input signal wavelengths of 1250 nm (Fig. S15) and 1350 nm (Fig. S16) for the ENZ nanostructure with a spacer thickness of 1549 nm. The pump wavelength is fixed at 1300 nm.

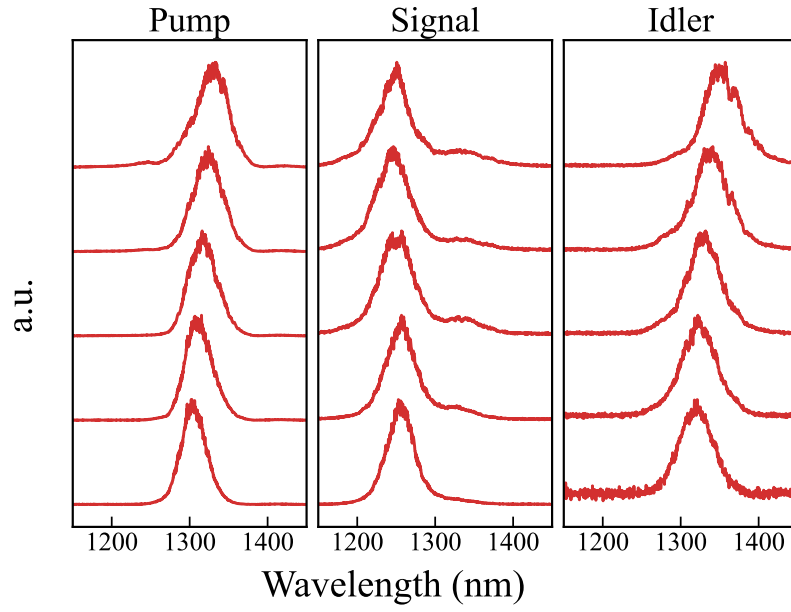


FIG. S15. The measured spectrum with input signal and pump wavelengths of 1250 nm and 1300 nm, respectively. The pump, signal, and idler spectra with the pump intensity from 10 to 100 GW/cm².

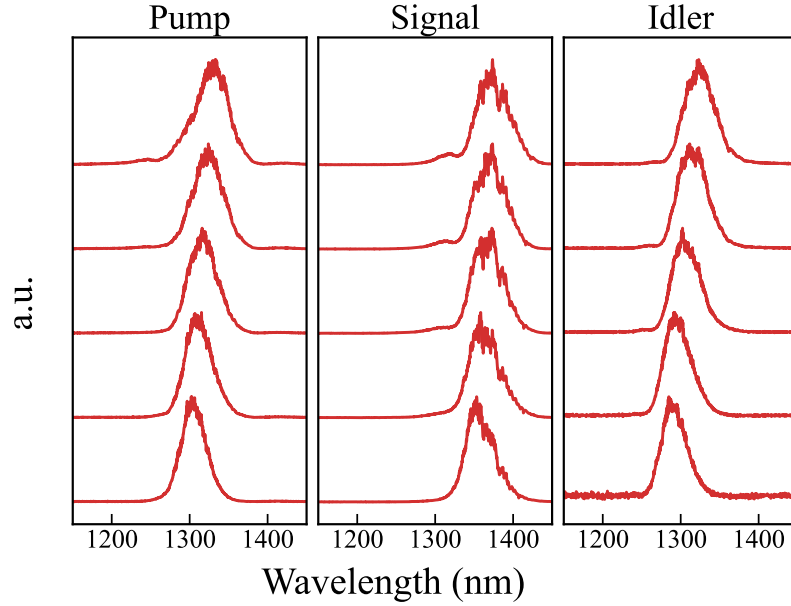


FIG. S16. The measured spectrum with input signal and pump wavelengths of 1350 nm and 1300 nm, respectively. The pump, signal, and idler spectra with the pump intensity from 10 to 100 GW/cm².

SUPPLEMENTAL NOTE 11: INTENSITY-DEPENDENCE ON NON-DFWM GENERATION FOR THE ENZ NANOSTRUCTURE

We measured the idler efficiencies of the ENZ nanostructure with a spacer thickness of 1549 nm as a function of pump intensity (GW/cm²) for various input signal wavelengths (Fig. S17). The pump wavelength is fixed at 1300 nm. A quadratic fit was applied to each case, with the results and fitting parameters presented in the sub-figure legends.

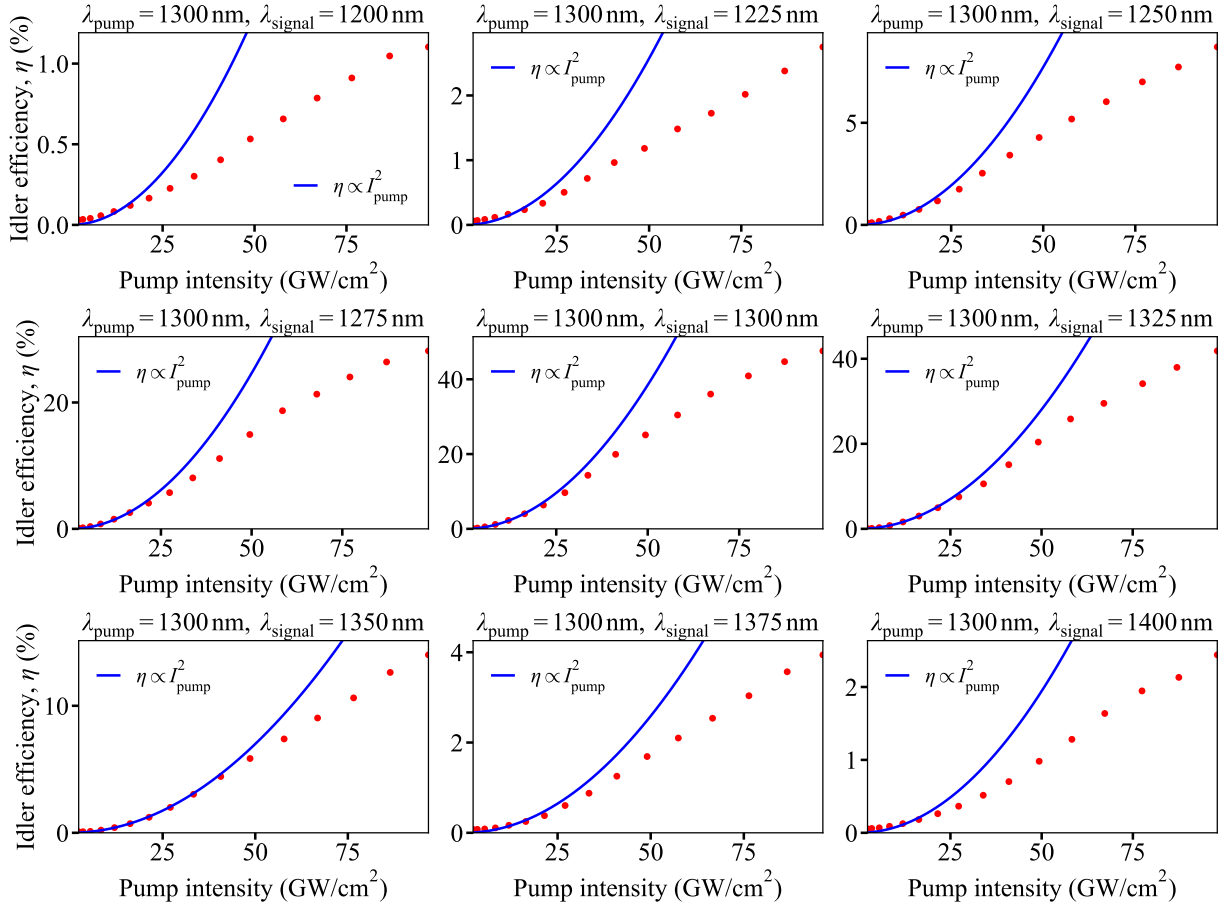


FIG. S17. **The intensity dependence for nDFWM efficiencies with different signal wavelengths.** The idler efficiencies as a function of pump intensity with the input signal wavelengths of 1200 nm, 1225 nm, 1250 nm, 1275 nm, 1300 nm, 1325 nm, 1350 nm, 1375 nm, and 1400 nm. The pump wavelength is maintained at 1300 nm.

SUPPLEMENTAL NOTE 12: HIGHER ORDER WAVE MIXINGS

The near infrared image of the diffraction orders observed for the ENZ nanostructure with a spacer thickness of 1549 nm is shown in Fig. S18a, while Fig. S18b shows a photograph of the diffraction pattern generated by the same ENZ nanostructure recorded on an infrared viewing card and captured using an iPhone camera. For the same pump intensity of 100 GW/cm² and signal intensity of 15 GW/cm², the near infrared image of the diffraction orders for a 310 nm thick ITO film is shown in Fig. S18c. Both images were recorded with pump and signal wavelengths of 1300 nm. The ENZ nanostructure displays diffraction orders up to twelve-wave mixing, whereas ITO shows only up to six-wave mixing.

Figure. S19 shows the measured efficiencies of the six-wave mixing (6WM) and eight-wave mixing (8WM) as a function of pump and signal intensities. The pump and signal wavelengths are both fixed at 1300 nm. The efficiencies are defined as the ratio of the generated idler power to the input signal power. The 6WM signal exhibits an approximately cubic dependence on pump intensity and a quadratic dependence on signal intensity. Similarly, the 8WM signal shows a fourth-order dependence on pump intensity and a cubic dependence on signal intensity. These observed scalings are consistent with higher-order nonlinear interactions enabled by the strong field enhancement in the ENZ nanostructure. At higher intensities, the efficiencies deviate from ideal power-law behavior, likely due to saturation effects. Under the experimental conditions considered, the 6WM efficiency reaches approximately 10%, while the 8WM efficiency is on the order of 2%. It is worth noting that the required pump intensities to observe higher-order modes are less than 100 GW/cm². Similar measurements conducted on conventional materials, such as BK7 glass, typically require pump intensities on the order of 1 TW/cm² [10, 11].

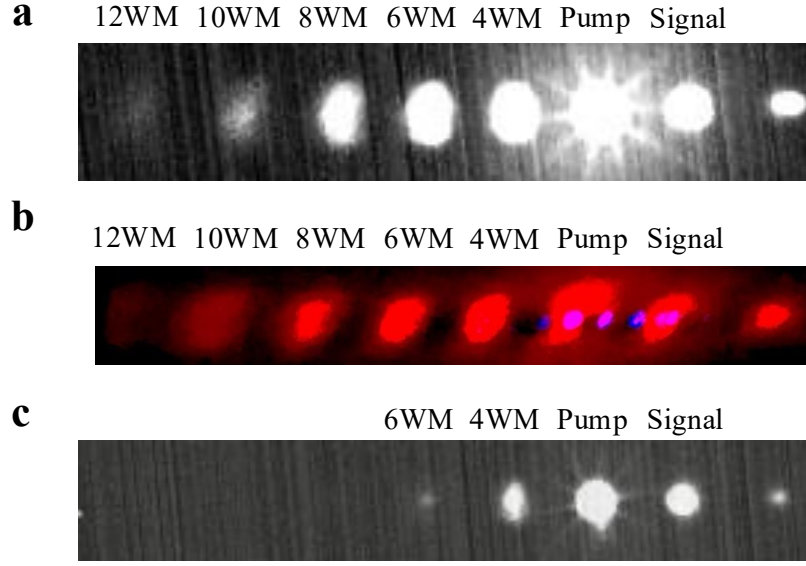


FIG. S18. **Images of higher-order wave-mixing diffraction orders.** **a**, Near-infrared image recorded using an infrared camera for the ENZ nanostructure with a spacer thickness of 1549 nm. **b**, Photograph of the diffraction pattern generated by the same ENZ nanostructure, projected onto an infrared viewing card and captured using an iPhone camera. **c**, Near-infrared image recorded using an infrared camera for a 310 nm thick ITO film. The pump and signal wavelengths were both 1300 nm with intensities of 100 GW/cm² and 15 GW/cm², respectively. The ENZ nanostructure exhibits diffraction orders up to twelve-wave mixing (12WM), whereas the monolithic ITO film exhibits diffraction orders up to six-wave mixing (6WM). The photograph in **b** provides a direct visual confirmation of the enhanced nonlinear wave-mixing response of the ENZ nanostructure.

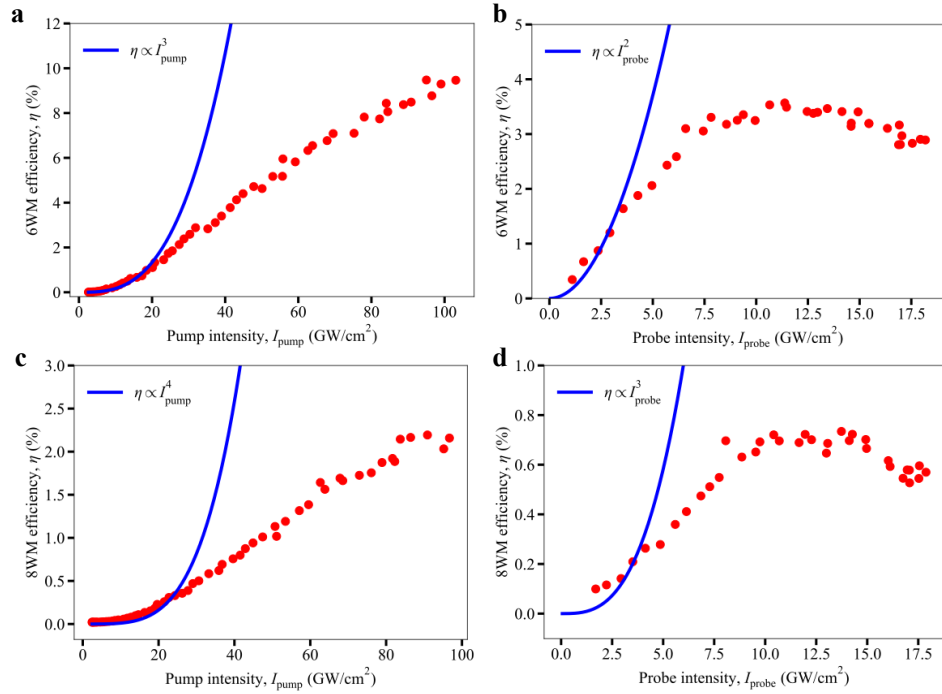


FIG. S19. **Six- and eight-wave mixing efficiencies.** (a) 6WM efficiency as a function of pump intensity, signal intensity is 12 GW/cm². (b) 6WM efficiency as a function of signal intensity, pump intensity is 40 GW/cm². (c) 8WM efficiency as a function of pump intensity, signal intensity is 12 GW/cm². (d) 8WM efficiency as a function of signal intensity, pump intensity is 40 GW/cm². Red symbols: experimental data. Blue lines: expected power-law scaling.

SUPPLEMENTAL NOTE 13: PERFORMANCE COMPARISON OF IDLER EFFICIENCY ON VARIOUS PLATFORMS

We compare the maximum idler conversion efficiency of our nanostructure with other reported works on idler (Fig. S20), such as bare ENZ materials [5, 6, 12], waveguides [13–16], nanostructures [17–23], photonic crystals [24], bulk optical materials [25–27], and Rubidium atoms [28].

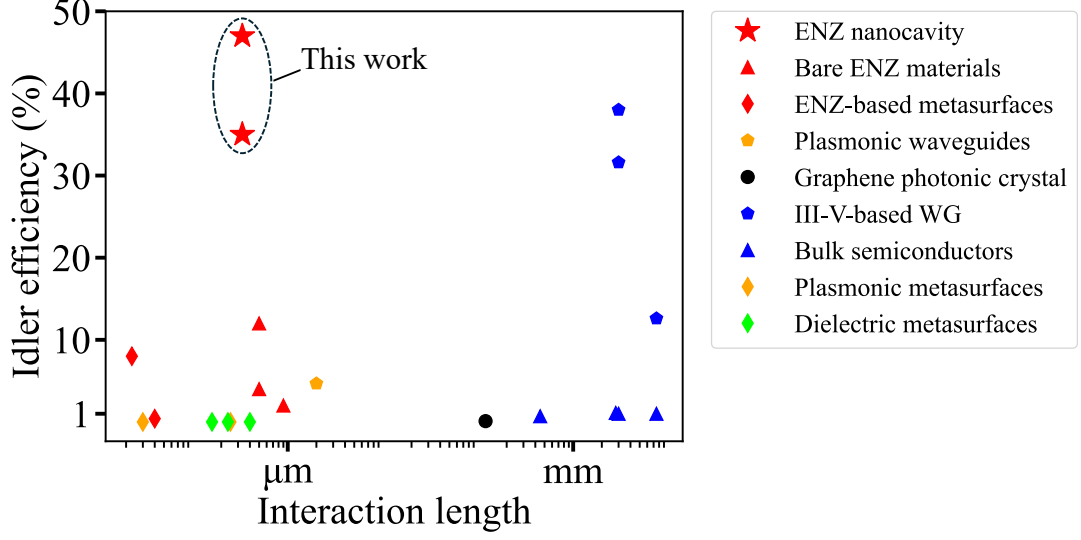


FIG. S20. **Comparison with other platforms for FWM generation.** FWM comparison of the maximum idler efficiency of various photonic platforms. The colors of the markers indicate the material, and their shapes indicate the device structure.

Orders of magnitude comparison with semiconductor-doped glass

To demonstrate the high nonlinearity of the ENZ nanostructure, wave-mixing conversion efficiencies are compared with those of a semiconductor glass. First, the measured 4WM, 6WM, 8WM conversion efficiencies of the 3 mm semiconductor glass with an input pump intensity of 0.1 MW/cm^2 are shown in the second column of table I [29]. The ENZ nanostructure is about 3–5 orders of magnitude higher than that of the semiconductor glass.

To directly compare the nonlinearity of the ENZ nanostructure with that of the semiconductor-doped glass, the glass conversion efficiencies are scaled to the same interaction length as the nanostructure (333 nm). Since the conversion efficiencies obey the scaling law of the interaction length ($\propto L^2$), the corresponding conversion efficiencies for 4WM, 6WM, and 8WM are $\sim 1.2 \times 10^{-11}$, $\sim 1.23 \times 10^{-13}$, and $\sim 5 \times 10^{-15}$, respectively. As observed, the conversion efficiencies reduce significantly. With the same interaction length, the 4WM conversion efficiency can be about 10 orders of magnitude higher than that of semiconductor-doped glass, and the higher-order wave mixing conversion efficiencies are even more extreme, where the 6WM and 8WM efficiencies can be 12 and 13 orders of magnitude higher, which shows that the ENZ nanostructure is highly nonlinear.

Conversion efficiency	3-mm semiconductor-doped glass	ENZ nanostructure
$\eta_{4\text{WM}}$	$\sim 1 \times 10^{-3}$	0.48
$\eta_{6\text{WM}}$	$\sim 1 \times 10^{-5}$	0.1
$\eta_{8\text{WM}}$	$\sim 4 \times 10^{-7}$	0.02

TABLE I. Comparison of semiconductor glass and ENZ nanostructure for wave mixing efficiencies.

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Chapter 5

Nonreciprocity in Epsilon-Near-Zero Dielectric Bilayer Structures

Overview

This chapter explores Berreman modes in ultrathin ENZ materials and their role in nonlinear nonreciprocity. While Chapter 1 introduced the physical origin of Berreman modes and ENZ nonlinearities, here I focus on how these effects can be used to produce nonreciprocal transmission in ITO–Si bilayer structures.

This project is a collaborative effort between the research groups of Professors Robert W. Boyd and Nader Engheta. Dr. Diego M. Solís and Professor Nader Engheta had earlier performed nonlinear numerical simulations predicting that ITO–Si bilayer structures would exhibit nonreciprocal transmission for sufficiently intense optical fields at oblique incidence angles [1]. Using the optimal device dimensions predicted by the nonreciprocity modeling, Dr. Shivashankar Vangala

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and Dr. Joshua Hendrickson from the US Air Force fabricated the sample.

In the next few sections, I first briefly introduce optical nonreciprocity and summarize the design principles of the ITO–Si bilayer. I then present the linear optical characterization of the fabricated bilayer structure, along with transfer-matrix-method (TMM) simulations, before finally showing the nonlinear nonreciprocal measurements. Since the fabricated dimensions differ slightly from the optimized design parameters, the comparison between experiment and theory presented in Ref. [1] focuses primarily on qualitative agreement in trends and operating regimes. A more accurate quantitative comparison requires updated nonlinear simulations using the fabricated sample parameters, which we have not yet obtained from our colleagues at the time of submission.

5.1 Introduction

The Lorentz reciprocity theorem, a fundamental principle in electrodynamics, implies that wave transmission through a linear, time-invariant medium is reciprocal [2–4]. In a two-port system, as shown in Fig. 5.1, this implies that interchanging the source and detector yields identical transmission characteristics, i.e., $|S_{12}|^2 = |S_{21}|^2$, where $|S_{ji}|^2$ denotes the transmission measured at port j when port i is excited. The formal requirements for reciprocity and its implications are discussed extensively in several review articles [5–9]. Breaking reciprocity is essential for the realization of magnet-free optical isolators and circulators—devices that protect laser sources and sensitive components from destabilizing back-reflections and enable signal routing in optical networks [10]. Consequently, achieving nonreciprocal transmission in compact, efficient geometries remains an essential challenge for the development of photonics technologies.

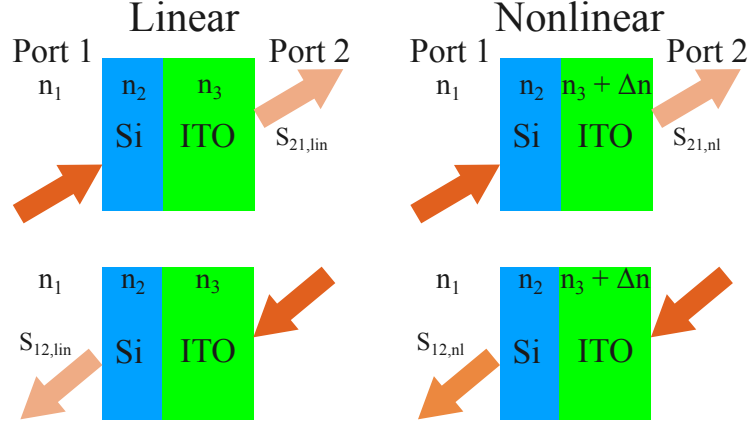


Figure 5.1: **Concept figures of nonlinear nonreciprocity.** Schematic of a nonlinear nonreciprocal bilayer. In the linear optical regime, the bilayer has the same transmission coefficient regardless of the excitation direction, $|S_{12}|^2/|S_{21}|^2 = 1.0$. When the intensity of the light beam is sufficiently strong, the refractive index changes from n_3 to $n_3 + \Delta n$. The resulting nonlinear transmission ratio, $\text{NTR} = |S_{12,\text{nl}}|^2/|S_{21,\text{nl}}|^2$ increases with pump intensity and saturates as the nonlinear response saturates. Here, S_{ji} denotes the transmission coefficient at port j when port i is excited.

Two primary approaches exist for achieving nonreciprocal transmission. The first exploits time-reversal-antisymmetric biasing, most commonly the magneto-optic Faraday effect, in which a static magnetic field renders the permittivity or permeability tensor asymmetric [11, 12]. This is the basis of commercial optical isolators; however, the requirement for a strong external magnetic field makes these devices bulky and difficult to integrate on a chip. The second approach relies on modulation of material properties, such as the refractive index, through acousto-optic, electro-optic, or optomechanical effects [13–22]. In this approach, the signal experiences an effectively linear but nonreciprocal response induced by an external traveling-wave drive. The

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drive field induces nonreciprocity through temporal or spatio-temporal modulations. An early example is the demonstration of a nonreciprocal contrast of 3 dB over a 200 GHz bandwidth at optical frequencies in a 10-mm-long silicon waveguide using electrically driven spatio-temporal modulation [23]. Temporal modulation of the refractive index can also be achieved using self or cross-phase modulation. In these cases, one leverages optical nonlinearities, such as the Kerr effect, to induce an intensity-dependent asymmetry in transmission [10, 24–31]. Since the nonlinear response depends on the local field distribution, to achieve nonreciprocity, the structures need to exhibit an asymmetric field distribution with respect to the excitation direction.

Nonreciprocal transmission ratios as high as 22–28 dB have been demonstrated in high- Q silicon microrings exploiting Kerr and thermal nonlinearities [32]. However, these devices are limited by narrow operating bandwidths, large footprints, and slow thermal response times. Improved response times have been achieved using carrier-based dynamics in photonic crystal structures, but at the cost of high insertion losses and similarly narrow bandwidths [33]. These limitations motivate the search for material platforms that provide both strong intrinsic nonlinearities and pronounced excitation direction-dependent field enhancement in simple geometries.

Recently, switchable Mie resonances of Silicon nanoresonators integrated on vanadium oxide thin film, a phase-change material, have been used to demonstrate a low-power, bias-free optical nonreciprocal transmission ratio of ~ 5 [34]. While nanoresonator architecture reduced the footprint, such platforms are limited by the response times of phase-transition dynamics. Sounas and Alù showed that nonlinear resonator-based isolators are subject to an inherent trade-off between transmission and achievable isolation [35, 36]. A separate but equally important constraint was identified by Shi, Yu, and Fan, who demonstrated that Kerr-based nonreciprocal devices obey a

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dynamic reciprocity relation. Although single-beam transmission may be asymmetric, simultaneous counterpropagating signals restore reciprocity, limiting the utility of such devices as true optical isolators [37]. Despite these demonstrations, the realization of nonreciprocal devices in metasurface geometry remains a significant area of interest in the photonics community.

Epsilon-near-zero (ENZ) materials—whose real permittivity vanishes at a characteristic frequency—offer a compelling route toward satisfying some if not all of the performance requirements described above. Materials such as indium tin oxide (ITO) exhibit exceptionally large nonlinear responses in their ENZ spectral region [38–40]. One of the sources of such large nonlinearity is the enhancement of the longitudinal electric field component in the ENZ medium. Consequently, in a judiciously engineered asymmetric layered geometry that shows reciprocal transmission in the linear optical regime, the continuity condition of the normal displacement field at the ENZ interfaces produces a strong enhancement of the normal electric field component (E_z) that depends on the excitation direction. While the direction-dependent field enhancement does not affect linear transmission, it makes the overall structure’s nonlinear optical response direction-dependent.

These considerations motivate the use of ENZ–dielectric bilayers, where strong longitudinal field enhancement and structural asymmetry can be achieved simultaneously in a simple ultrathin geometry without the need for external biasing. In this chapter, I present a simple nonlinear nonreciprocal device that leverages the large optical nonlinearity of indium tin oxide in its ENZ region.

Compact nonreciprocal devices operating at optical frequencies remain a key challenge for photonic systems. In this work, I demonstrate nonreciprocity in a reciprocal free-space epsilon-

5.2. *LINEAR RESPONSE AND FIELD ASYMMETRY OF THE ITO–SI BILAYER*

near-zero (ENZ)–dielectric bilayer composed of indium tin oxide (ITO) and silicon. The total thickness of the structure is only ~ 271 nm, contains no magnetic material, and is reciprocal in the regime of linear optics. In the nonlinear regime, the nonreciprocal response arises from the direction-dependent asymmetric enhancement of the electric field in the ENZ layer. The measured nonreciprocal transmission ratio reaches ~ 3 dB over a 4 THz bandwidth in the telecom C-band, limited by the laser source’s spectral range. The overall bandwidth is potentially broader. The simplicity of the bilayer geometry and its CMOS compatibility suggest a viable route toward all-optical nonlinear nonreciprocal nanostructures.

5.2 Linear response and field asymmetry of the ITO–Si bilayer

The ability of a simple bilayer including a realistic ENZ material to demonstrate nonreciprocal behaviour rests on two key elements: 1) An ENZ thin film has a Berreman or Brewster mode to which light can couple at oblique incidence and show significant field enhancement 2) The coupling efficiency to this mode and the consequent loss of transmission through the device is highly susceptible to the ENZ thin film’s large nonlinear optical responsiveness. If the bilayer dimensions are selected to account for the light phase at each interface, this can facilitate field enhancement in the ENZ film and coupling to the Berreman mode for light incident from one side of the bilayer, while limiting such enhancement for light incident from the other side. In this section, I consider this asymmetry and the consequent opportunity for nonreciprocity.

To understand the origin of nonlinear nonreciprocity in the fabricated structure, we first analyze the linear optical response of the ITO–Si bilayer using the transfer matrix method (TMM). In

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performing TMM, we treat the substrate as an incoherent layer to suppress Fabry–Pérot fringes associated with it. Only the ITO and Si layers are treated coherently to capture the interference and field buildup within the ITO. In this way, we preserve the correct Fresnel coupling into the bilayer while avoiding artificial substrate resonances in the calculated spectra and field profiles. The calculations are performed using the experimentally measured optical constants and the fabricated thicknesses.

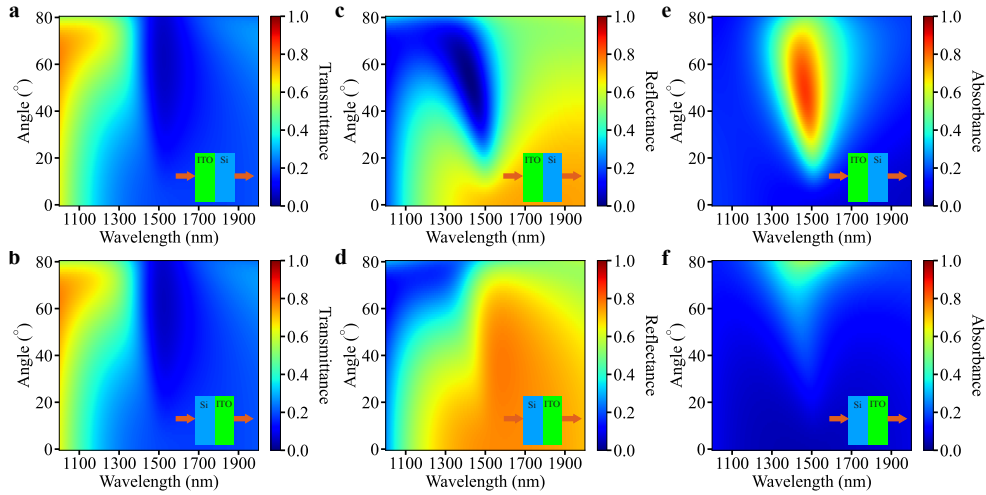


Figure 5.2: **Linear response of the fabricated ITO–Si bilayer.** Top row: transmittance, reflectance, and absorbance for excitation from the ITO side. Bottom row: corresponding quantities for excitation from the Si side. The panels compare forward and backward excitation directly, showing reciprocity in transmission but strong asymmetry in reflection and absorption.

Figure 5.2 shows the angular and spectral dependence of transmittance, reflectance, and absorbance for excitation from both directions in the ENZ spectral region of ITO. Figure 5.2a and b show identical transmittance of the structure when excited from either direction, confirming

5.2. LINEAR RESPONSE AND FIELD ASYMMETRY OF THE ITO–SI BILAYER

that the ITO–Si bilayer structure is reciprocal in the linear regime, as it should be for any linear time-invariant system. However, the reflectance and absorbance shown in Figure 5.2(c–f) differ significantly in the ENZ spectral region of ITO based on the excitation direction. This does not violate reciprocity, since reflection and absorption are not required to be identical for opposite excitation directions in an asymmetric multilayer. The asymmetric absorbance observed originates from direction-dependent coupling to the Berreman mode supported by the ENZ layer. The maximum absorption of 0.853 occurs at 1465 nm for an angle of incidence of 49° in Figure 5.2e.

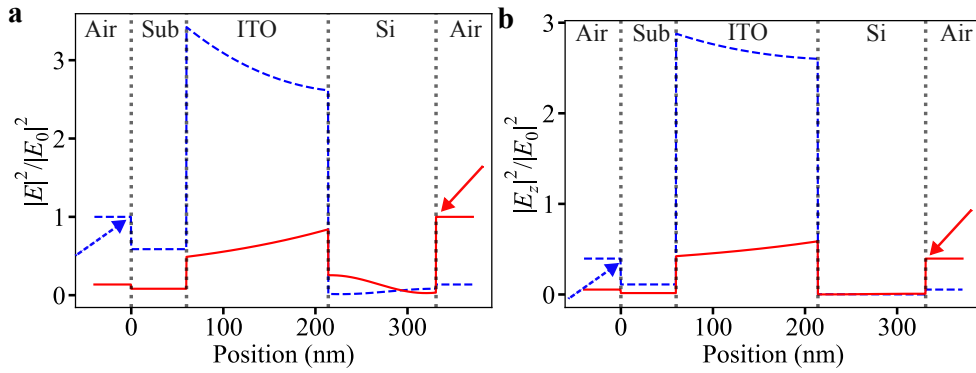


Figure 5.3: **Electric-field profiles inside the ITO–Si bilayer for opposite excitation directions at 39° incidence and 1468 nm.** **a**, Total field and **b**, longitudinal field enhancement across the ITO–Si bilayer structure. The blue dotted line indicates forward excitation, where the light is first incident on the ITO side, and the red line indicates backward excitation, where the light is incident on the Si layer first. These conditions correspond to the maximum forward longitudinal field enhancement identified from the TMM analysis.

The quantity most relevant to nonlinear response is not the absorption itself, but the field enhancement within the ITO layer, especially the longitudinal field enhancement. For obliquely incident

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p -polarized light, the continuity of the normal displacement field at the interfaces enhances the longitudinal field component in the ENZ layer. Because the bilayer is asymmetric, this enhancement differs for the two excitation directions. Figure 5.3 shows the normalized spatial distribution of $|E|^2$ and $|E_z|^2$ across the structure for the two excitation directions at a particular angle and wavelength. When excited from the ITO side, the field is strongly localized within the ENZ layer, whereas excitation from the Si side results in a significantly weaker field. This asymmetry follows from the boundary condition on the normal displacement field, $\epsilon_1 E_{z,1} = \epsilon_2 E_{z,2}$, which produces a strong enhancement of E_z inside the ENZ layer when $\text{Re}(\epsilon_{\text{ITO}})$ approaches zero.

This asymmetry in the field enhancement observed in the ITO layer is what determines the structure's nonreciprocal nonlinear response. A sufficiently intense beam can experience different nonlinear transmissions based on the excitation direction, even though the corresponding linear transmission is identical. At the same time, the linear field map alone is not sufficient to explain the measured nonlinear transmission ratios quantitatively, because the nonlinear response also depends on how the ITO permittivity changes with intensity and on how this change affects the coupling to the Berreman mode. So, nonlinear simulations are essential to properly model the spectral and angular regions where the bilayer structure exhibits nonreciprocity.

Solís and Engheta theoretically predicted nonreciprocal transmission in an ITO–Si bilayer structure [1] using both nonlinear finite-difference frequency-domain (FDFD) methods for steady-state analysis as well as nonlinear finite-difference time-domain (FDTD) methods to analyze the nonreciprocal behavior under pulsed excitation [41, 42].

Before that, the ITO and Si thicknesses were optimized using transfer-matrix methods (TMM)

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to maximize absorption and the longitudinal electric field within the ITO layer, particularly for excitation from the ITO side. This behavior is associated with efficient coupling to the Ferrell–Berreman mode supported by the ITO film [40, 43]. Detailed description of the ENZ modes and Ferrell–Berreman mode is given in Section. 1.4.4. In TMM, they treated ITO as a Drude material with an ENZ wavelength around 1240 nm and realistic loss. The complex permittivity at the ENZ is $\epsilon_{\text{ENZ}} \approx 0.35i$. They identified that maximum absorption and field asymmetry occur for a 100 nm ITO layer and an 80 nm Si film. The spectral and angular positions of maximum field enhancement are associated with efficient coupling to the mode. In contrast, for maximum absorption, impedance matching of the structure (the pseudo-Brewster condition) also plays a role, leading to a slight offset between the two.

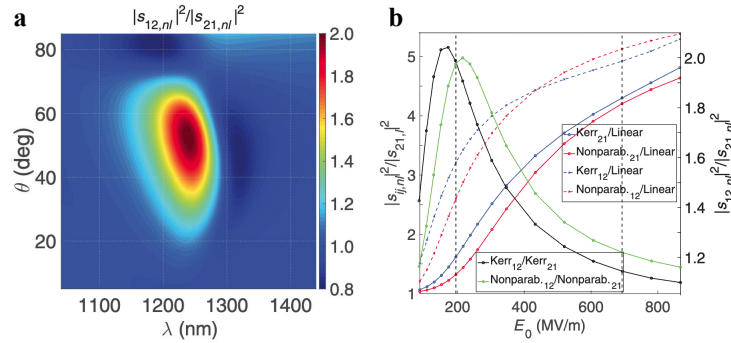


Figure 5.4: **Nonlinear transmission ratio (NTR) modeled using finite-difference simulations in an optimized ITO–Si bilayer structure.** **a**, Angular and spectral dependence of the NTR. **b**, Intensity dependence of the NTR showing a maximum value of ~ 2 . Panels (a) and (b) are adapted from Figs. 2(f) and 3(b) of Ref. [1], reproduced with permission from the American Physical Society.

Fig. 5.4a shows the spectral and angular dependence of the nonlinear transmission ratio (NTR =

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$|S_{12,\text{nl}}|^2/|S_{21,\text{nl}}|^2$) obtained using nonlinear FDFD simulations. NTR values of ~ 2 are achieved near the ENZ wavelength for a wide range of incidence angles around 45° – 55° . Here, they assume an instantaneous Kerr nonlinearity, which accounts for self-phase modulation.

ITO nonlinearities, as described in Sec. 1.4.2, are associated with hot-electron nonlinearities, which are delayed and arise from the nonparabolicity of the conduction band. Therefore, for pulsed excitation simulations, they use nonlinear FDTD. The corresponding intensity-dependent response (Fig. 5.4b, black and green curves, where black corresponds to instantaneous response and green corresponds to delayed nonlinearities) shows that the NTR increases with input intensity, reaches a maximum, and then decreases at higher intensities, highlighting a key prediction that the nonreciprocal response is optimized at a finite input intensity rather than monotonically increasing. This reduction is attributed to the nonlinear detuning of the ENZ condition and reduced coupling to the Berreman mode.

These results establish nonlinear nonreciprocal transmission in a 180 nm-thick ITO–Si bilayer structure numerically. This simulation work establishes a direct connection between field asymmetry and nonlinear nonreciprocity and shows how to optimize the bilayer thicknesses to maximize this nonreciprocal transmission. The key aspect of the design is to efficiently couple to the Berreman mode from one excitation direction, leading to maximum field asymmetry between the two excitation directions and, consequently, a nonreciprocal transmission ratio of ~ 2 .

5.3. FABRICATION AND LINEAR CHARACTERIZATION

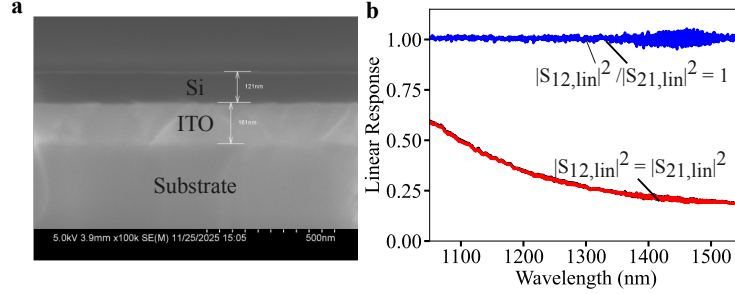


Figure 5.5: **Fabricated ITO–Si bilayer and linear response.** **a**, SEM cross-section of the bilayer on the substrate. The measured thicknesses are 161 nm for ITO and 121 nm for Si, with an estimated uncertainty of about 4% from the SEM critical-dimension measurement. **b**, Linear transmission spectra measured from both excitation directions, showing reciprocal response in the linear regime. The overlap of the forward and backward transmission spectra confirms that the structure remains reciprocal under low-intensity excitation.

5.3 Fabrication and linear characterization

Encouraged by these predictions, we set out to demonstrate nonreciprocal transmission in ENZ–dielectric bilayer structures experimentally. Thin films of ITO and silicon at appropriate thicknesses for FE within the ITO layer were deposited on a double-sided polished (DSP) glass substrate by DC magnetron sputtering using methods developed for a near-infrared wideband perfect absorber previously reported in [44].

Figure 5.5a shows the scanning electron microscope (SEM) cross-section of the bilayer, confirming the ITO and Si thicknesses of 154 nm and 117 nm, respectively, with an estimated ~4% uncertainty in the SEM critical-dimension measurement. The optical constants of the films were

5.4. *NONLINEAR RESPONSE AND EXPERIMENTAL DEMONSTRATION*

confirmed using spectroscopic ellipsometry and subsequently used in the linear TMM simulations. The ITO's ENZ crossing, absorption, and the thin film thicknesses deviate from the design values considered in Ref. [1]. Therefore, the spectral and angular locations of maximum field enhancement and absorption are expected to shift accordingly.

Linear transmission measurements were performed using broadband illumination. Figure 5.5b shows the linear transmission spectra of the sample, measured from both excitation directions using white light and the ratio of two transmissions as blue dots. As expected for a linear measurement, the measured transmission is identical in both directions, yielding an NTR of 1, confirming that the structure is reciprocal in the linear regime. In addition, the agreement between the measured transmission spectra and the TMM predictions provides confidence that the modeling framework captures the key physical features of the fabricated structure. This allows linear simulations to reliably predict operating regions with strong field asymmetry, which, in turn, guide the nonlinear measurements discussed in the following section.

5.4 Nonlinear response and experimental demonstration

As we did not have access to nonlinear FDTD simulations to predict the NTR of our device as a function of wavelength and incident angle, we instead used our linear TMM measurements to find the parameter space of greatest field enhancement within the ITO thin film. We presume that this is a rough facsimile of where nonreciprocity will be most pronounced. Figure 5.6a shows the thickness-averaged normal electric-field intensity inside the ITO layer for excitation from port 2 (ITO side), calculated using TMM. The maximum field enhancement of 2.70 is achieved

5.4. NONLINEAR RESPONSE AND EXPERIMENTAL DEMONSTRATION

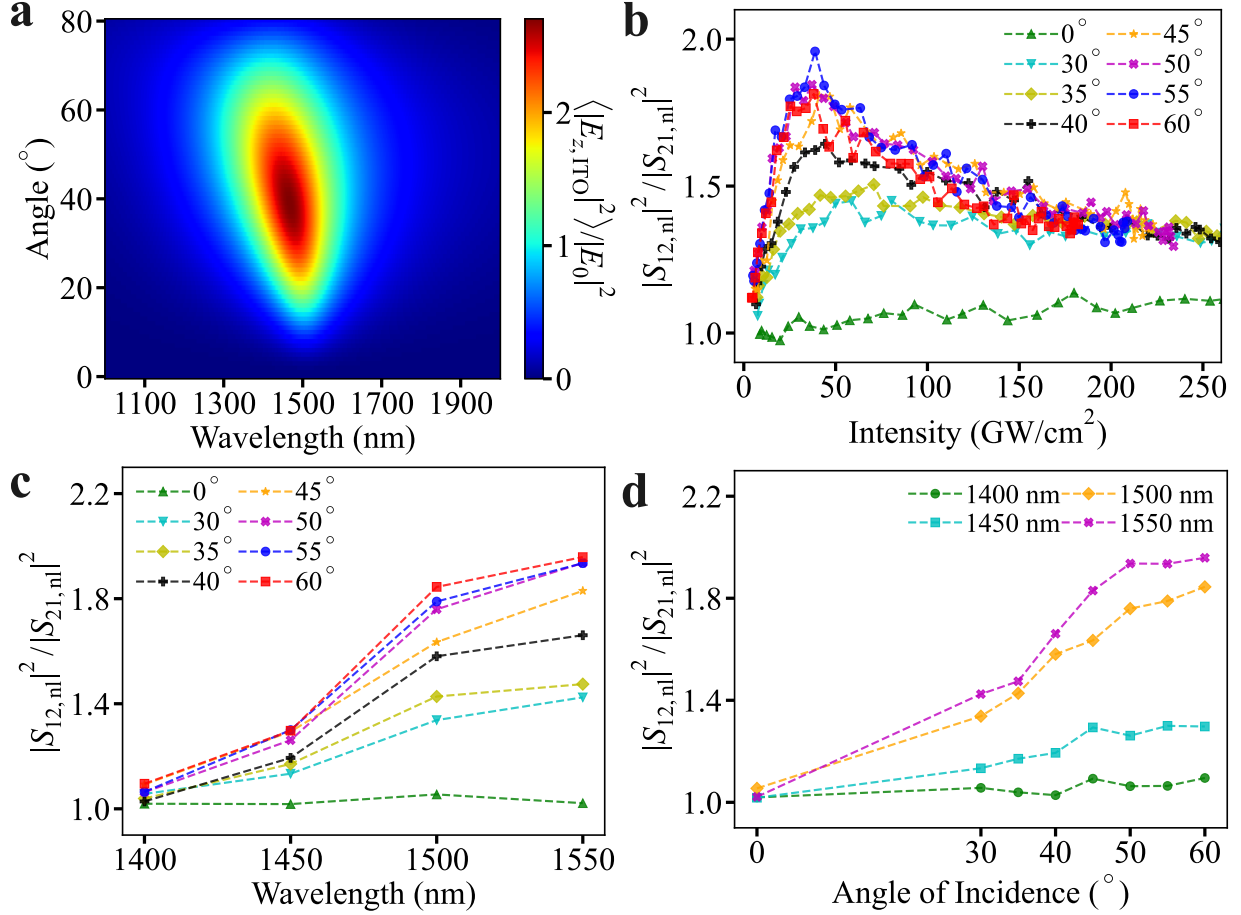


Figure 5.6: **Nonlinear response and experimental nonreciprocity.** **a**, Thickness-averaged normal electric-field intensity inside the ITO layer for excitation from port 2 (ITO side), calculated using TMM. **b**, Experimental nonreciprocal transmission ratio (NTR) as a function of intensity for different angles of incidence at 1500 nm. **c**, Spectral dependence of the maximum NTR. **d**, Angular dependence of the maximum NTR. Panel (a) identifies the linear operating regime used to guide the nonlinear measurements, while panels (b)–(d) show the experimentally observed nonlinear response.

5.4. NONLINEAR RESPONSE AND EXPERIMENTAL DEMONSTRATION

at 1468 nm and 39.0°. Based on the TMM analysis, we performed nonlinear transmission experiments in the angular and spectral region where the field asymmetry inside the ITO layer is maximized. We note that the nonlinear behavior depends not only on the initial field enhancement but also on the intensity-dependent change in the ITO permittivity, which modifies the coupling to the Berreman mode.

We next experimentally investigate the nonlinear transmission response under asymmetric field enhancement conditions. Nonlinear transmittance measurements were performed using ~100 fs pulses generated by a Ti:Sapphire laser (TOPAS Prime, Spectra Physics) pumping an optical parametric amplifier, providing tunable wavelengths in the 1100–1550 nm range. We then varied the laser pulse intensity using a half-wave plate mounted on rotational stages and a Glan–Taylor polarizer. The laser pulse is set to p-polarization. The beam waist of the pulse is adjusted to 42 μm using plano-convex lenses. The laser intensity was varied from 1 to 250 GW/cm^2 , and the incidence angle was varied from 0 to 60°. Next, the transmitted beam from the sample is measured by an InGaAs photodetector (Newport 98D-IG-OD3R). Once the result is recorded, we rotated the sample 180° and performed the same set of experiments to measure the transmitted beam from the backside of the sample. Both sets of results were analyzed to assess the sample's nonreciprocity behavior.

Figure 5.6b shows the experimentally measured nonreciprocal transmission ratio (NTR), defined as $|S_{12,\text{nl}}|^2/|S_{21,\text{nl}}|^2$, as a function of input intensity for different angles of incidence at the ENZ wavelength of ITO, 1500 nm. At normal incidence, the response is almost reciprocal despite the increase in intensity. This can be explained by the absence of significant field asymmetry in the structure and the negligible coupling to the Berreman mode.

5.4. *NONLINEAR RESPONSE AND EXPERIMENTAL DEMONSTRATION*

Under oblique angles, however, the NTR increases with intensity, reaches a maximum value, and then decreases at higher intensities as predicted by the simulations shown in Fig. 5.4[1]. The increase in NTR with intensity follows from the ITO's nonlinear response. The direction-dependent field enhancement identified in the TMM analysis leads to different nonlinear transmission values for different excitation directions. The subsequent decrease in NTR at higher intensities indicates a reduction in coupling to the Berreman mode due to the intensity-induced modification of the ENZ condition. In addition, saturation effects in the ENZ region of ITO also contribute to reducing NTR values [38]. The maximum NTR is observed between 45° and 55° , in agreement with the angular region of strongest field enhancement predicted by the TMM analysis (Figure 5.6a). This further confirms that the nonlinear response depends on both the field distribution and the intensity-induced modification of ITO's optical properties.

To characterize the spectral and angular bandwidth of the nonreciprocal response, we repeated the intensity-dependent measurements across the ENZ spectral region by varying the pump wavelength and the angle of incidence. The maximum NTR values extracted at each wavelength and angle are shown in Fig. 5.6c and Fig. 5.6d, respectively. The spectral response peaks near the ENZ wavelength, while the angular response peaks between 45° and 55° . Laser tuning bandwidth limitations and practical limits on incident angle prevent a full characterization of the wavelength angle parameter space, but the measured NTR results do show reasonable qualitative agreement with the field enhancement in the ITO in Fig. 1.5a, and thus are a reasonable experimental confirmation of this model for a nonreciprocal bilayer.

We note that the measured NTR reaches values of ~ 2 (~ 3 dB). This magnitude is limited by intrinsic losses in ITO and is consistent with the upper bound reported in Ref. [1]. Overall, the

5.5. DISCUSSION AND OUTLOOK

experimental results show three key features: (i) reciprocal linear response, (ii) nonlinear non-reciprocity at high intensities, and (iii) saturation and subsequent reduction of the nonreciprocal response.

5.5 Discussion and Outlook

To place the experimental results in context, we compare them with the nonlinear simulations reported for the optimized ITO–Si bilayer structure in Ref. [1]. The simulated NTR map predicts a maximum response near 50° and at wavelengths close to the ENZ region, as shown earlier in Fig. 5.4a. Experimentally, due to limitations of the laser source, the spectral and angular bandwidths were explored only up to 1500 nm. Still, the measured trends follow the spectral and angular regions associated with field enhancement in the ITO layer, consistent with numerical simulations that predict the maximum NTR in the ENZ spectral region.

Similarly, the experimental NTR as a function of intensity shown in Fig. 5.6b follows the same trend as the simulation in Fig. 5.4b, indicating that the underlying nonlinear mechanism is consistent with the model. A more quantitative comparison would require nonlinear simulations using the measured thicknesses and experimentally extracted optical constants of the fabricated sample, which are not included in this chapter.

In conclusion, the experimental results establish nonlinear nonreciprocity in a simple ITO–Si bilayer geometry. The nonreciprocity stems from the directional asymmetry in the longitudinal electric field within the ENZ layer, driven by boundary conditions at the interface. The observed

5.5. DISCUSSION AND OUTLOOK

nonreciprocal transmission ratio (NTR) is ~ 2 (~ 3 dB), consistent with the theoretical upper limit predicted by Solís and Engheta [1]. The NTR increases with intensity, and at higher intensities it decreases due to modifications in the ENZ condition and a resulting reduction in coupling to the Berreman mode, which is responsible for the enhanced field confinement. The nonreciprocal response spans roughly ~ 4 THz bandwidth covering the telecom C-band.

We note that, as with all nonlinearity-based nonreciprocal devices, the dynamic reciprocity constraint [37] implies that the asymmetric transmission observed here under single-beam excitation does not constitute true optical isolation under simultaneous bidirectional signal conditions. Nevertheless, this work provides the first experimental validation of ENZ-assisted nonreciprocal transmission in the telecommunications band in an ultracompact (~ 271 nm) bilayer platform. The simplicity of the bilayer geometry, the CMOS-compatible constituent materials, and the absence of any external bias or magnetic field suggest that ENZ–dielectric structures are promising candidates for compact nonreciprocal photonic elements.

The performance of ENZ-based nonreciprocal metasurfaces can be improved by increasing the field enhancement and reducing material loss in the ITO layer. Possible approaches include using dielectric [45] or plasmonic metasurfaces [46, 47], high- Q lattice resonances [48], or phonon polaritons [49]. Another direction is to exploit the strong time-refraction effects in ITO and use the spectro-temporal response of ENZ materials to separate signals in frequency and momentum space [50–52].

Future work involves performing full nonlinear simulations using the fabricated structure parameters to enable a more direct comparison with the experimental results and further validate the

observed trends.

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Chapter 6

Dynamic coherent perfect absorption in nonlinear metasurfaces

Contribution Statement

This work represents the first project I pursued after joining Professor Robert W. Boyd's group in Fall 2019. The study focuses on coherent perfect absorption in plasmonic metasurfaces integrated with ITO, which was introduced to me during initial discussions with Dr. Rasoul Alaei. Dr. Alaei trained me in COMSOL simulations, and together we conducted all numerical studies of a plasmonic metasurface on ITO to demonstrate coherent perfect absorption and its dynamic tunability via optical pumping.

The concept and initial design of the metasurface were developed by Dr. Rasoul Alaei. Dr. Rasoul Alaei prepared the first draft of the manuscript. I contributed to subsequent revisions alongside Professor Boyd, refining both the presentation and the interpretation of the results.

My contributions to the work are summarized below:

1. Performing numerical simulations of plasmonic metasurfaces on ITO using COMSOL (primary contributor alongside Dr. Rasoul Alaei).
2. Contributing to the revision of the manuscript (secondary contributor after Dr. Rasoul Alaei).
3. Revising the manuscript (all authors).

Optics Letters

Dynamic coherent perfect absorption in nonlinear metasurfaces

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In this Letter, we propose a tunable coherent perfect absorber based on ultrathin nonlinear metasurfaces. A nonlinear metasurface is made of plasmonic nanoantennas coupled to an epsilon-near-zero material with a large optical nonlinearity. The coherent perfect absorption is achieved by controlling the relative phases of the input beams. Here, we show that the optical response of the nonlinear metasurface can be tuned from a complete to a partial absorption by changing the intensity of the pump beam. The proposed nonlinear metasurface can be used to design optically tunable thermal emitters, modulators, and sensors. © 2020 Optical Society of America

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An electromagnetic wave carries energy. In many applications in optics (e.g., solar cells, thermal emitters, optical modulators, optical sensors, and optical data processors), it is desirable to absorb light completely [1–5]. In principle, complete light absorption occurs when both reflection and transmission vanish at the same frequency. Perfect absorbers have been proposed after the invention of radar by Salisbury, also known as Salisbury screens [1]. A Salisbury perfect absorber consists of an absorbing layer on top of a metal ground plane separated by a dielectric spacer. Such absorber relies on the destructive interference of the reflected light between the absorbing layer and the metal ground plane (by varying the thickness of the dielectric spacer) and suppression of the transmitted light (due to optically thick metal ground plane).

It is well known that an optically thin metasurface with only an electric dipole response maximally absorbs 50% of the impinging light [2,4–6]. Recently, metasurface perfect absorbers have been introduced using subwavelength resonant particles with *electric and magnetic* responses [4,5,7,8]. These absorbers are thin compared to the operating wavelength and can fully absorb the light without a ground plane. An alternative approach to perfectly absorbing light in an optically thin metasurface with only an electric dipole response is coherent perfect absorber (CPA) by using the interference of two/multiple incoming beams [9–11]. In the CPA, it is essential to choose the intensities appropriately and the relative phases of the two input beams to achieve the perfect absorption. The position of

the metasurface in the standing wave, produced by the interference of two coherent input beams, determines the amount of absorption.

Tunable perfect absorbers have been experimentally and theoretically realized by using tunable materials such as graphene [12–15], liquid crystals [16], and phase-change materials [17–20]. Recently, a new class of low-index materials, called epsilon-near-zero (ENZ) materials, has attracted much attention because of its large nonlinear response [21–26]. As the name indicates, ENZ materials are the materials in which the real part of the permittivity goes to zero at a particular frequency [see Fig. 2(a) for the indium tin oxide (ITO) film]. ENZ materials exhibit a huge electric field enhancement, as well as large nonlinearity at the ENZ frequency [27]. In particular, ITO and aluminum-doped zinc oxide (AZO) as ENZ materials are used to achieve *tunable* antennas and optical switches [21,22,24,26,28]. Perfect absorption has been achieved using the ENZ materials in the linear regime [29–33]. A nearly coherent perfect absorber has been achieved by using Kerr optical nonlinearities in the AZO thin films [34].

In this Letter, we propose an *ultrathin nonlinear* coherent perfect absorber based on an ITO metasurface. In the absence of a pump beam, we show that the metasurface exhibits coherent perfect absorption when illuminated from both sides. The CPA condition, i.e., $t^2 = r_F r_B$, occurs when one of the eigenvalues of the scattering matrix is zero [9]. We demonstrate that the absorber is tunable when applying a third beam (pump beam) with high intensity (see Fig. 1).

The underlying physics of a coherent perfect absorber can be understood using the scattering-matrix formalism [35,36]. The relation between the input **a** and output **b** waves can be described by **b** = **S****a**, where

$$\mathbf{a} = \begin{pmatrix} a_F \\ a_B \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} b_F \\ b_B \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} r_F & t_B \\ t_F & r_B \end{pmatrix}. \quad (1)$$

r_F and r_B are the reflection coefficients, t_F and t_B are the transmission coefficients from forward and backward directions, respectively [36]. Coherent perfect absorber occurs when the output waves vanishes, i.e., **b** = **0** and that is **b** = **S****a**_{CPA} = **0**. This means that at least one eigenvalue of the **S** is zero, and the eigenvector is the CPA eigenmode, i.e., **a**_{CPA}. For symmetric

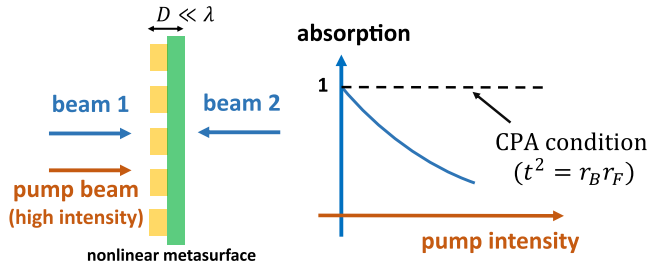


Fig. 1. Main idea of this Letter: a tunable coherent perfect absorber (CPA). Sketch of an ultrathin (i.e., $D \ll \lambda$, where D is the thickness of the metasurface) nonlinear metasurface illuminated by two counterpropagating incident beams. In the absence of a pump beam, the two coherent beams (i.e., beam1, beam2) lead to the CPA when the reflected and transmitted lights destructively interfere on each side of the metasurface. The CPA occurs when Fresnel coefficients satisfy $t^2 = r_B r_F$. Note that single-beam illumination leads to partial absorption [see Figs. 2(e) and 2(f)]. In the presence of the pump, one can modify the absorption by increasing the pump intensity.

structure, the eigenvectors are $(1, \pm 1)$, i.e., the symmetric and antisymmetric input beams. Note that the CPA condition is the time reverse of the lasing [9,11].

Figure 2(b) shows the schematic of the proposed tunable coherent perfect absorbers. The structure is composed of a gold metasurface 30 nm in thickness on a glass substrate. The ITO layer is sandwiched between the metasurface and the glass substrate. The permittivity of ITO is expressed as $\varepsilon = \varepsilon_\infty - \omega_p^2 / (\omega^2 + i\gamma\omega)$, where $\omega_p = 2.67 \times 10^{15}$ rad/s, $\varepsilon_\infty = 3.9$, and $\gamma = 2.32 \times 10^{14}$ Hz [see Fig. 2(a)]. The transmission spectrum is calculated in Fig. 2(d) for single-beam illumination (forward and backward directions) using a numerical finite element solver (COMSOL Multiphysics). Note that the forward and backward transmissions are identical, i.e., $T = T_F = T_B$ because the system is reciprocal [37]. The structure exhibits strong coupling between two resonances, i.e., the bulk-plasma mode of the ENZ layer and the fundamental mode of the plasmonic nanoantennas [22,38]. The resonances of the coupled system can be calculated from the eigenvalue problem, i.e., $H\psi = \hbar\tilde{\omega}_{u,l}\psi$, where ψ is the eigenstate of the coupled system, and H is defined as [39]

$$H = \hbar \begin{pmatrix} \tilde{\omega}_{\text{ITO}} & \Delta \\ \Delta & \tilde{\omega}_{\text{MS}} \end{pmatrix}, \quad (2)$$

where $\tilde{\omega}_{\text{ITO}} = \omega_p - i\gamma$ and $\tilde{\omega}_{\text{MS}} = \omega_{\text{LSP}} - i\gamma_{\text{LSP}}$. ω_{LSP} and γ_{LSP} are resonance frequency and linewidth of the localized surface plasmon (LSP) mode of the plasmonic antennas in the absence of the ITO layer, respectively [extracted from Fig. 2(c)]. Δ is the coupling between the bulk-plasma mode of the ITO and the fundamental mode of the metasurface. The coupling Δ is extracted from the simulation of the coupled system. The eigenvalues of the coupled systems are given by

$$\tilde{\omega}_{u,l} = \frac{1}{2} \left(\tilde{\omega}_{\text{MS}} + \tilde{\omega}_{\text{ITO}} \pm \sqrt{(\tilde{\omega}_{\text{MS}} - \tilde{\omega}_{\text{ITO}})^2 + 4\Delta^2} \right). \quad (3)$$

The red and white dashed lines in Fig. 2(d) show the resonance of the metasurface without the ITO and the ENZ wavelength of ITO, respectively. Using Eq. (3), we calculate the resonance wavelengths of the coupled system [see black dashed lines in Fig. 2(d)]. There is a very good agreement between the

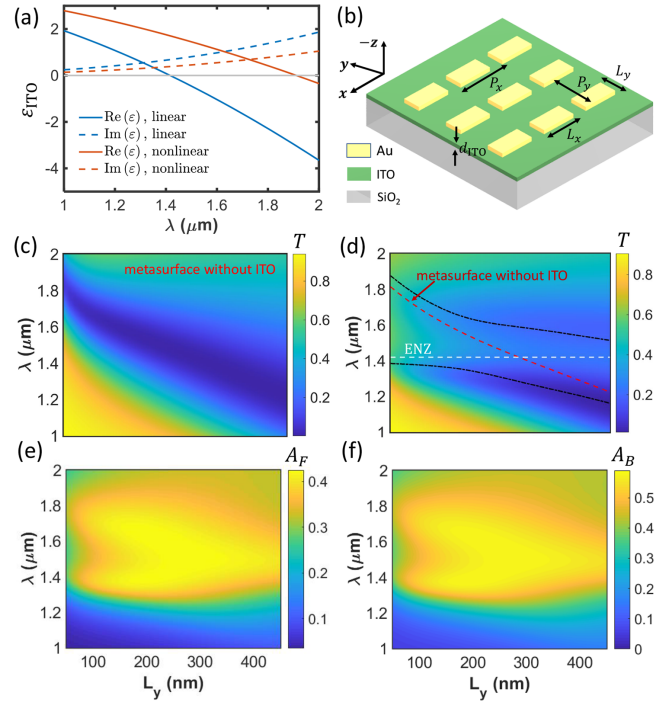


Fig. 2. Single-beam excitation: (a) real and imaginary parts of the linear ($\omega_p = 2.67 \times 10^{15}$ rad/s) and nonlinear ($\omega_{p1} = 2 \times 10^{15}$ rad/s) relative permittivities of the ITO film. (b) Sketch of the tunable perfect absorber consisting of a gold metasurface on top of the ITO-coated SiO_2 . The incident plane wave is polarized along the x -axis. (c) Transmission of the metasurface without ITO film as a function of wavelength and dimension of the gold antennas, i.e., L_y . (d) Same as (c) with the ITO film. Note that the dashed lines depict the resonance wavelength of the ENZ, i.e., λ_{ENZ} (white), and the resonance wavelength of the metasurface without ITO, i.e., λ_{MS} (red). Using Eq. (3), the resonance wavelengths of the coupled system, i.e., $\lambda_{u,l}$ can be calculated (see the black dashed lines). (e) and (f) Absorption ($A_{F/B} = 1 - T - R_{F/B}$) for forward ($\mathbf{k}_F = k_0 \mathbf{e}_z$) and backward ($\mathbf{k}_B = -k_0 n_{\text{SiO}_2} \mathbf{e}_z$) illuminations, respectively. The geometrical parameters of the metasurface are $d_{\text{ITO}} = 23$ nm, $P_x = P_y = 650$ nm, and $L_x = 450$ nm. The thickness of the gold nanoantenna is 30 nm.

simulation (using COMSOL) and the semi-analytical model [using Eq. (3)].

Figures 2(e) and 2(f) show the absorption from the forward and backward directions, i.e., $A_{F/B} = 1 - T - R_{F/B}$. $R_F = |r_F|^2$ and $R_B = |r_B|^2$ are reflection from forward and backward, respectively. First, it can be seen that the absorptions (or reflections) are *not* symmetric for the two opposing irradiation directions. The asymmetric reflections/absorptions can be understood from the fact that the system is *not* invariant under space inversion [40–42]. Note that an optically thin metasurface consisting of an electric dipole antennas in an isotropic and homogeneous medium can only absorb 50% of the light [2,4,5]. Our proposed asymmetric metasurface is ultrathin, i.e., $\lambda_{\text{res}}/t_{\text{MS}} \approx 30$, where λ_{res} is the resonance wavelength, and t_{MS} is the overall thickness of the metasurface (gold antennas and ITO). Following the approach in [2,5,6], we found that the maximum absorption for forward illumination is $A_F^{\text{max}} = n_{\text{air}} / (n_{\text{air}} + n_{\text{SiO}_2}) \approx 0.4$ [see Fig. 2(e)]. Similarly, the maximum backward absorption reads as $A_B^{\text{max}} = n_{\text{SiO}_2} / (n_{\text{air}} + n_{\text{SiO}_2}) \approx 0.6$ [see Fig. 2(f)]. Interestingly, we get $A_B^{\text{max}} + A_F^{\text{max}} = 1$.

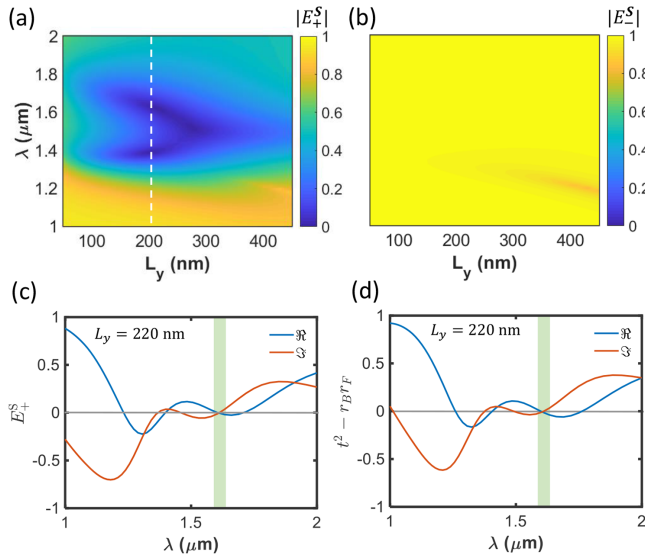


Fig. 3. Coherent perfect absorber condition: (a),(b) Modulus of eigenvalues of the scattering matrix S as a function of wavelength and dimension of the gold antennas. (c) Real and imaginary parts of the eigenvalue of the S -matrix as a function of wavelength for $L_y = 220$ nm. (d) $t^2 - r_F r_B$ as a function of wavelength. The CPA condition occurs at $1.6 \mu\text{m}$. Note that this condition is approximately satisfied over a wide range of wavelengths due to the broadband response of the coupled system.

To find the condition for the coherent perfect absorption, we calculate the two eigenvalues of the scattering matrix, i.e., $E_{\pm}^S = \left(-C_{FB} \pm \sqrt{C_{FB}^2 - 4(r_F r_B - t^2)} \right) / 2$, where $C_{FB} = -(r_F + r_B)$. Thus, the CPA condition, i.e., $t^2 = r_F r_B$ occurs when one of the eigenvalues of S matrix is zero, i.e., $E_{+}^S = 0$. Figures 3(a) and 3(b) show the modulus of the eigenvalues of $E_{\pm}^S$ matrix as a function of frequency and length of the antenna L_y . It can be seen that only one of the eigenvalues, i.e., E_{+}^S , vanishes, e.g., at $L_y = 220$ nm [see the white dashed line in Fig. 3(a)]. Figure 3(c) shows that the real and the imaginary parts of the eigenvalue E_{+}^S are zero at $1.6 \mu\text{m}$ (see the green shadow). At this wavelength, Fresnel coefficients also satisfy $t^2 = r_F r_B$ [see the green shadow in Fig. 3(d)]. Note that the CPA condition is approximately satisfied over a wide range of wavelength due to the broadband response of the coupled system [3,22,38,43]. Therefore, we expect to achieve a nearly broadband CPA for the two-beam illuminations. From now on, we will only consider the metasurface with $L_y = 220$ nm because this geometry satisfies the CPA condition, i.e., $t^2 = r_F r_B$.

Let us now consider the CPA configuration [see the two-beam illumination in Fig. 4(a)]. For the two beams, the joint absorption can be defined as [44]

$$A = 1 - \frac{|b_1|^2 + |b_2|^2}{|a_1|^2 + |a_2|^2}. \quad (4)$$

For lossless systems, absorption is zero $A = 0$, and unity $A = 1$ for the CPA. Figure 4(b) shows the joint absorption for the two-beam illumination as a function of the relative phase of the input beams, i.e., ϕ . By varying the relative phase of the two-beams from 0 to π , the absorption of the metasurface goes

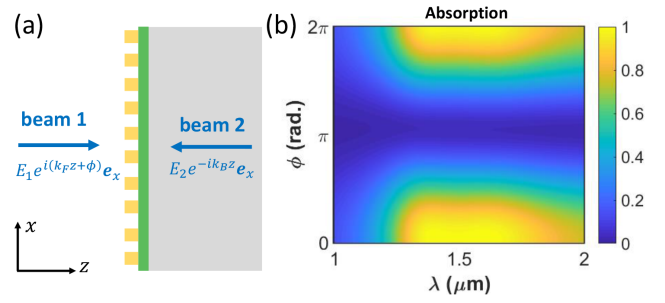


Fig. 4. Two counterpropagating incident beams: (a) schematic representation of the CPA metasurface illuminated by two input beams with low intensities. (b) Absorption as a function of the wavelength and the relative phase between input beams, i.e., ϕ . The CPA occurs when two beams are in phase, i.e., $\phi = 0, 2\pi$. The absorption is nearly zero when two input beams are out of phase, i.e., $\phi = \pi$.

from perfect absorption to nearly zero absorption, while keeping the two beam intensities constant. Note that we used different amplitudes for the incident beams, i.e., $E_2 = 0.86E_1$, which is related to the CPA eigenvector of the $\mathbf{a}_{\text{CPA}}$. In other words, the Fresnel coefficients are different because the system is not symmetric. Nearly perfect absorption occurs over a large range of frequencies, i.e., $1.3 - 1.75 \mu\text{m}$ [see also the white dashed line in Fig. 3(a), which depicts the CPA condition]. Figure 4(b) shows that when two beams are out of phase, the absorption is nearly zero because of the vanishing incidence field inside the metasurface.

Next, we consider the effect of a pump beam on the absorption of the proposed nonlinear metasurface. It has been experimentally shown that the refractive index of the ITO depends on the intensity of the pump beam [21,28]. At the high optical intensity regime, ITO's response can be described by the Drude model [21,22,45]. In this model, the plasma frequency of the ITO decreases as the intensity of light increases [21,22,45]. In our simulation, we changed the plasma frequency in the Drude model to model ITO's nonlinearities. Figure 5

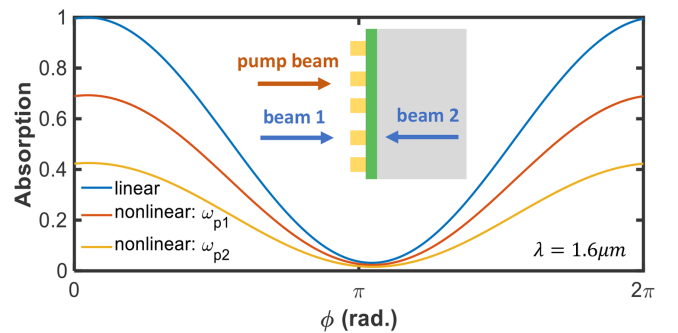


Fig. 5. Two counterpropagating input beams with a pump beam: (a) absorption as a function of the relative phase between two beams at the wavelength $1.6 \mu\text{m}$. The inset shows the sketch of a tunable coherent perfect absorber illuminated by two low-intensity counterpropagating input beams and a high-intensity pump beam. The pump beam changes the refractive index of the ITO. In the nonlinear simulation, we assumed that $\omega_{p1} = 2 \times 10^{15}$ rad/s [see the permittivity of the ITO film in Fig. 2(a)] and $\omega_{p2} = 1.33 \times 10^{15}$ rad/s. Considering the field enhancement in the ITO layer, these plasma frequencies approximately correspond to pump intensities in the range of $I_0 = 1 - 10 \text{ GW/cm}^2$. These are typical intensities that have been reported in the nonlinear experiment with ITO samples [38].

shows the absorption as a function of the relative phase between two beams, i.e., ϕ with and without the pump beam. It can be seen that the absorption is significantly decreased by applying the pump beam (from unity to 0.4) when the relative phase of the two-beams is zero. At $\phi = \pi$, the absorption is almost independent of the pump beam because of vanishing incidence field inside the metasurface. Our proposed CPA is ultrathin ($\lambda_{CPA}/30$, where λ_{CPA} is the CPA wavelength), and its optical response can be switched within a subpicosecond timescale by employing an ultrafast optical pump beam [21].

In conclusion, we have shown that coherent perfect absorption can occur for a metasurface made of optical nanoantennas coupled to an ENZ material. In particular, we have demonstrated that the absorption of the metasurface can be tuned by applying a high-intensity pump beam. Our results can be employed to design tunable thermal emitters, optical modulators, optical sensors, and optical data processes.

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Chapter 7

Conclusions

The overarching theme of this thesis has been to explore and further enhance the large optical nonlinearities of transparent conducting oxides (TCOs), particularly in the epsilon-near-zero (ENZ) region of indium tin oxide (ITO). The work presented in this thesis investigates several third-order nonlinear phenomena like time-varying parametric amplification, enhanced wave mixing, nonreciprocal transmission, and coherent perfect absorption. Chapter 1 briefly introduces optical nonlinearities in ENZ materials, with particular emphasis on the large and ultrafast refractive index modulation and the resulting pump–probe delay–dependent frequency shifts — time refraction. The chapter also introduces ENZ and Ferrell–Berreman modes in ultrathin ENZ materials and discusses how the large longitudinal field enhancements associated with these modes can be accessed.

In Chapter 2, we investigated the consequences of time-refraction in epsilon-near-zero materials. We analyze the nonlinear change in transmission of a weak probe beam in the presence of a strong pump using the formalism of conventional two-beam coupling in $\chi^{(3)}$ materials. Two-beam coupling describes the coherent energy transfer between two frequency-nondegenerate

beams and depends linearly on the nonlinear refractive index and pump intensity. Here, we show that in ENZ materials, coherent energy transfer does not require an initial frequency dependence or chirp in the pulses.

In ENZ materials, the pump-induced refractive-index modulation produces a pump–probe delay–dependent frequency shift in the probe, thereby modifying its nonlinear transmission. We show, both theoretically and experimentally, that in a 620 nm thick ITO film, coherent energy transfer between frequency-degenerate pulses exhibits a quadratic dependence on $n_2 I$. Although this mechanism had been theoretically predicted, its experimental observation is enabled by the large and ultrafast refractive-index modulation in ENZ materials, which produces strong time-varying optical effects over a subwavelength interaction length. As a result, we observe probe amplification in a subwavelength-thick indium tin oxide film, despite the material’s strong absorption. These results demonstrate that the strong nonlinear response of ENZ materials enables parametric processes that differ from conventional two-beam coupling and opens a pathway for ultrashort-pulse amplification using time-varying nanophotonic platforms.

Chapters 3 and 4 explore nanophotonic structures designed to further enhance nonlinear optical interactions in ENZ materials. In particular, we designed an ITO-based Gires–Tournois nanocavity (ITO–SiO₂–Au) in which the ITO layer acts both as the nonlinear medium and as a partially reflecting mirror. We show that engineering the spacer thickness to support a resonant cavity mode in the ENZ spectral region excites the Brewster mode with strong longitudinal electric-field enhancement within the nonlinear material, ITO.

By reducing the intrinsic absorption of ITO in numerical simulations (modeled as a decrease

in the imaginary part of the permittivity), we demonstrate coupling between the Brewster mode associated with the ENZ region of the ITO layer and the cavity mode determined by the spacer thickness. In experimentally fabricated samples, however, the intrinsic absorption of ITO causes these resonances to merge into a single broad dip in the reflection spectrum. We demonstrate how optical pumping modulates the refractive index and spectrally redshifts the resonance condition and the Brewster mode of the nanocavity. This spectral redshift is more pronounced in the Brewster mode, which is primarily confined within the ITO layer, than in the cavity resonance mode, which is mainly confined to the spacer layer. As a result, the hybrid resonance splits into two distinct modes, with the Brewster mode redshifting by approximately 130 nm. We numerically validate the spectral evolution of these modes by varying the ITO plasma frequency in the nanocavity using the transfer-matrix method. Pump–probe delay measurements reveal the temporal dynamics of the nanocavity modes with an on–off contrast of approximately 25 dB. These results illustrate the potential of ENZ nanocavities for ultrafast all-optical switching.

In Chapter 4, we exploit the strong longitudinal electric-field enhancement of these angle-dependent modes to enhance nonlinear wave-mixing processes. We demonstrate four-wave mixing efficiencies of approximately 45% when frequency-degenerate pump and signal beams are used. To our knowledge, these efficiencies are among the highest reported in 2 μm -scale nanostructures. When the pump and signal are frequency-nondegenerate, the device supports four-wave mixing over approximately 70 nm spanning the telecommunications O-band. From these measurements, we infer that the effective nonlinear response time of ITO is on the order of tens of femtoseconds. This high efficiency arises from the enhanced longitudinal electric fields within the ITO layer of the nanocavity, which increase the nonlinear interaction for all

participating waves.

Chapters 5 and 6 investigate Ferrell–Berreman and ENZ modes in ultrathin ITO films. In Chapter 5, we study nonlinear nonreciprocal transmission in an ENZ–dielectric bilayer consisting of indium tin oxide and silicon. By engineering the structure to couple maximally to the Berreman mode of ITO, we experimentally demonstrate a nonreciprocal transmission ratio of approximately 2 in a ~ 271 nm thick structure without applying any external magnetic or electrical bias. The designed structure is reciprocal in the linear regime. Under intense illumination, excitation from opposite directions leads to asymmetric longitudinal electric-field enhancement within the ITO layer due to the different excitation conditions of the Berreman mode. This asymmetry results in a direction-dependent nonlinear response. We also examined the spectral and angular bandwidth of this effect. We found that the nonreciprocity is confined to the ENZ spectral region, spanning roughly 4 THz across the telecommunications C-band.

In Chapter 6, we investigate plasmonic metasurfaces patterned on ultrathin ITO films. By designing plasmonic resonances near the ENZ wavelength, we achieve strong coupling between the localized surface plasmon resonance of the nanoantennas and the ENZ mode of a 23 nm ITO film. Using this platform, we demonstrate coherent, perfect absorption with two counterpropagating beams and show that the absorption response can be dynamically tuned by optically pumping the ITO layer and thereby modifying its plasma frequency.

In addition to the results presented in Chapters 2–6, a significant portion of my PhD research involved designing, fabricating, and characterizing a variety of plasmonic and dielectric metasurfaces. While many of these platforms remain exploratory, they illustrate the wide range

of possibilities that arise when ENZ materials are combined with nanophotonic architectures. Several of these directions remain ongoing and continue to motivate further experimental and theoretical work. The appendix of this thesis describes a few published metasurface works to which I contributed.

Overall, the results presented in this thesis show that ENZ materials provide a promising platform for studying strong nonlinear optical interactions at the nanoscale. While ENZ materials already exhibit unusually large nonlinear responses due to their near-zero permittivity, the work presented here demonstrates how engineering nanostructures with ENZ materials can further enhance optical nonlinearities.

Outlook and future directions

The work presented in this thesis motivates further experimental investigations. One immediate direction is a more systematic exploration of nonlinear wave-mixing processes in the ENZ nanocavity introduced in Chapter 4. The observed four-, six-, and eight-wave mixing conversion efficiencies indicate that the ENZ nanocavity provides an efficient platform for nonlinear optical interactions. Effects such as real-time optical holography [1] and imaging through scattering media [2], which rely on nonlinear wave mixing, may benefit from the enhanced conversion efficiencies demonstrated here. In addition, wave-mixing processes involving harmonic generation could be investigated within the same cavity platform.

Future work could explore how the nonlinear response depends on parameters such as the ITO

thickness, spacer thickness, and cavity geometry. Optimizing these parameters may further enhance field confinement and wave-mixing efficiency. A major challenge underlying many of these efforts is the intrinsic optical loss of ENZ materials, which limits both field buildup and interaction length.

The enhanced third-order nonlinearities in the ENZ nanocavity may also enable wave-mixing processes involving structured light. In particular, nonlinear interactions involving orbital angular momentum (OAM) beams provide another promising direction. In such interactions, conservation of orbital angular momentum requires that the generated idler carry an OAM determined by the OAM states of the pump and signal beams. Furthermore, the observation of high-order wave-mixing processes raises the possibility of generating multiple OAM orders simultaneously. At oblique incidence, the combination of structured-light excitation and ultrafast refractive-index modulation may enable the exploration of spatiotemporal nonlinear phenomena in ENZ materials.

The large stimulated four-wave mixing conversion efficiencies demonstrated in Chapter 4 also motivate the investigation of spontaneous four-wave mixing in ENZ nanophotonic structures. Previous theoretical work has shown that measurements of stimulated four-wave mixing can be used to infer the behavior of spontaneous four-wave mixing [3]. The strong conversion efficiencies observed in the nanocavity, therefore, indicate that photon-pair generation may be achievable in subwavelength ENZ platforms. ENZ nanocavities may therefore provide a compact platform for photon-pair generation, quantum frequency conversion, and related quantum nonlinear optical processes.

Although ITO has served as the primary ENZ material throughout this thesis, the underlying

enhancement mechanisms are not restricted to transparent conducting oxides. Polar dielectrics exhibit an ENZ response near longitudinal-optical phonon resonances and can provide significantly lower losses in the mid-infrared. Investigating Berreman-mode and cavity-enhanced nonlinearities in such materials would help determine whether the concepts developed in this thesis can be extended to other ENZ platforms and spectral regions [4, 5].

More broadly, the results presented in this thesis show that engineered electromagnetic environments can significantly enhance nonlinear optical interactions in ENZ materials. Continued development of ENZ nanocavities, metasurfaces integrated with ENZ films, and hybrid resonant structures may provide new opportunities to selectively enhance specific nonlinear processes and access regimes that are difficult to realize in unstructured ENZ films.

Personal reflection

After six years of working in Professor Robert Boyd’s group, ENZ nonlinearities continue to excite me as much as when I first joined. One of the most rewarding aspects of this research has been seeing how a relatively simple physical idea—that the permittivity approaching zero can dramatically enhance optical nonlinearities—can lead to a wide range of new phenomena and device concepts.

I am particularly interested in exploring how ENZ materials can be used in emerging areas such as analog optical computing, nonlinear signal processing, integrated photonic devices, and time-varying photonic systems such as photonic time crystals. The ideas and experimental platforms developed during this work will contribute to these directions and encourage further exploration of ENZ materials in nonlinear nanophotonics.

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Appendix A

Fourier-engineered plasmonic lattice resonances

Contribution Statement

This work was carried out shortly after I joined Professor Robert W. Boyd's group in 2019, during which I became interested in plasmonic metasurfaces supporting high-Q surface lattice resonances. While my initial project focused on coherent perfect absorption in ITO-based metasurfaces, I simultaneously began learning nanofabrication techniques under the supervision of Dr. Orad Reshef.

After completing my cleanroom training at the University of Ottawa, I shadowed Dr. Orad Reshef to learn the fabrication workflow for high-Q plasmonic metasurfaces. This training took place during the fabrication of the devices reported in this work, allowing me to gain hands-on experience with the fabrication protocol.

Following fabrication, I aligned the optical setup and performed the linear transmission measurements of the metasurfaces, which contributed to the experimental results presented in the publication.

My contributions to the work are summarized below:

1. Performing linear optical characterization of the metasurface samples (primary contributor).

Fourier-Engineered Plasmonic Lattice Resonances

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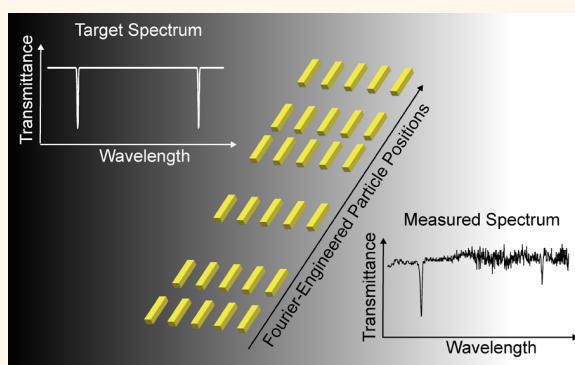
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Supporting Information

ABSTRACT: Resonances in optical systems are useful for many applications, such as frequency comb generation, optical filtering, and biosensing. However, many of these applications are difficult to implement in optical metasurfaces because traditional approaches for designing multiresonant nanostructures require significant computational and fabrication efforts. To address this challenge, we introduce the concept of Fourier lattice resonances (FLRs) in which multiple desired resonances can be chosen *a priori* and used to dictate the metasurface design. Because each resonance is supported by a distinct surface lattice mode, each can have a high quality factor. Here, we experimentally demonstrate several metasurfaces with flexibly placed resonances (e.g., at 1310 and 1550 nm) and *Q*-factors as high as 800 in a plasmonic platform. This flexible procedure requires only the computation of a single Fourier transform for its design, and is based on standard lithographic fabrication methods, allowing one to design and fabricate a metasurface to fit any specific, optical-cavity-based application. This work represents a step toward the complete control over the transmission spectrum of a metasurface.

KEYWORDS: plasmonics, metasurfaces, lattice resonances, nanoparticle arrays, nanophotonics



Plasmonic nanoparticles are essential tools for the manipulation of light beams in metasurfaces because of the flexibility of the placement of their localized surface plasmon resonances (LSPRs).¹ The LSPR wavelength can be easily tailored since it is highly dependent on the size and the shape of the nanoparticle.² Additionally, LSPRs confine light in the nanoscale, leading to significant local-field enhancements.³ Thanks to these desirable properties, many applications have been realized in a broad range of research fields such as optical filtering,^{4,5} harmonic generation,⁶ and biosensing.⁷ However, the applications of LSPRs are limited by the intrinsic absorption loss of metals; the quality-factor of LSPRs is low (*Q*-factor < 10).^{8,9} One method to improve the *Q*-factor of resonant plasmonic systems is to consider instead collective optical responses of multiple nanoparticles in a periodic lattice arrangement; such metasurface-scale responses are known as surface lattice resonances (SLRs).^{9–12} Unlike the LSPR, the SLR wavelength is defined by the periodicity of the positions of the nanoparticles in a periodic lattice, and this collective response has a relatively high *Q*-factor. For example, our recent work has experimentally demonstrated a *Q*-factor of 2340 around an operating wavelength of 1550 nm.¹¹

In addition to improving the *Q*-factor of a lattice response, it is also highly desirable to be able to freely choose the resonance wavelengths of the metasurface.^{13,14} The reason is simple: carefully tailoring multiple resonances in a metasurface allows one to customize a metasurface to specific applications, such as frequency comb generation,^{15,16} ultrasensitive biosensing,¹⁷ and fluorescence enhancements.¹⁸ For example, methods have been proposed to tune the resonance wavelength by manipulating the dimensions of multiple particles in a single cell,¹⁹ through plasmonic hybridization,²⁰ and using bound-state-in-the-continuum (BIC) modes.²¹ In metasurface systems, several methods have been studied to generate and tailor multiple lattice resonances, such as utilizing multiple materials,²² adding cladding layers to induce Fabry–Pérot SLR modes,¹² removing nanoparticles periodically,²³ using all-

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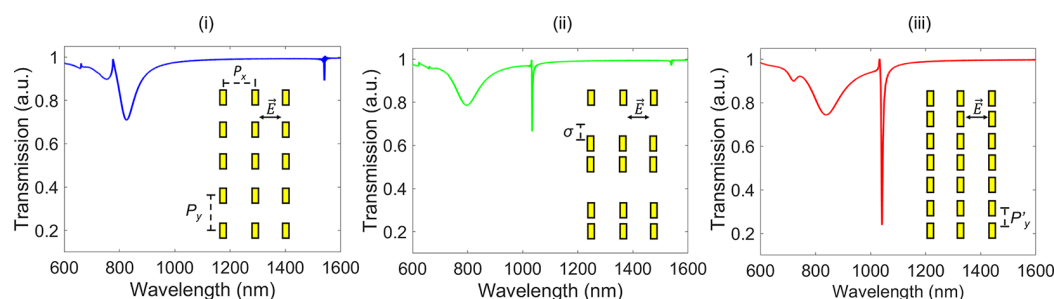


Figure 1. Bipartite Surface Lattice Resonance modes. The transmission profiles of three different lattice arrangements (i), (ii), and (iii) with their corresponding schematic drawings (see the inset figures). These lattice arrangements are made of rectangular nanoparticles, where P_y or P_y' and P_x are the lattice periodicity in the y -axis and x -axis, respectively. The incident electric field is polarized along the x -axis. (i) and (iii) are periodic arrays with lattice constants of P_y and P_y' , respectively. For the modulated lattice arrangement (ii), every second row of particles in the array in (i) is translated by spacing $\sigma = P_y/3$. Such a system resembles the array of (iii) but with vacancies.

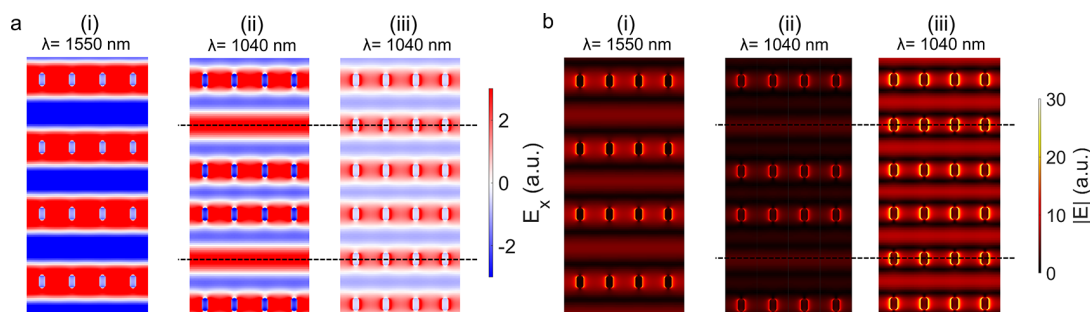


Figure 2. Near-field profiles of the lattice modes. (a) The normalized x -polarized electric field profiles of lattice arrangements from Figure 1, their respective SLR resonances of 1550 nm for (i) and 1040 nm for (ii) and (iii). The vacancies in every second row of the unit cell in (ii) are aligned with every second row of the particles of the unit cell in (iii) (the black dashed line). The electric fields in (ii) resemble those of (iii), indicating that a similar mode is being excited. (b) The electric field amplitude profiles of the lattice arrangements, showing the field enhancement at the resonances. These results also demonstrate that all of the SLR modes possess a field enhancement within the same order of magnitude.

dielectric Mie-resonance metasurfaces,²⁴ and superlattice arrays.²⁵ Each of these methods can support multiple resonance modes; however, they are all limited in the spectral position or number of these resonances. Some methods have been developed that can define any number of resonances in flexible locations in a metasurface. In this work, we tackle this issue by exploiting a different approach: by breaking the lattice periodicity, we show that we can simultaneously introduce multiple lattice resonances with tunable resonance wavelengths. With this knowledge, we introduce and experimentally demonstrate the concept of Fourier lattice resonances (FLRs), which are a natural generalization of SLRs that can support multiple lattice resonances at desired operation wavelengths.

RESULTS AND DISCUSSION

Interpretation of Fourier Lattice Resonances (FLRs).

For conceptual clarity, we begin by exploring how perturbations in translational symmetry introduce resonances. This demonstration helps interpret the physical origin of FLRs. Note that the main goal of this manuscript is *not* to reintroduce bipartite lattices,^{26–29} but to motivate the theory that we will develop later on for FLRs. Consider a metasurface consisting of rectangular gold nanoparticles with a periodic lattice arrangement. The lattice is embedded in a homogeneous background of silica glass ($n \sim 1.45$), with particle dimensions of $L_x = 110$ nm and $L_y = 180$ nm and periodicities of $P_x = 500$ nm and $P_y = 1063$ nm (see the inset in Figure 1(i)). The predicted transmission spectrum for an x -polarized beam is calculated by the finite-difference time-domain (FDTD)

method and is shown in Figure 1(i). The LSPR mode of the metasurface occurs at an operating wavelength of 830 nm, and the SLR is at 1550 nm ($\lambda_{\text{SLR}} \approx nP_y$). Next, we break the symmetry of the rectangular lattice by displacing every second row of particles by a distance $\sigma = P_y/3$ (see the inset in Figure 1(ii)). The calculated transmission profile of the metasurface is altered by this modulation (Figure 1(ii)): an additional collective resonance arises at 1040 nm. The origin of this resonance is clear when looking at Figure 1(iii), where we show a rectangular lattice of periodicity $P_y' = 2P_y/3$; the altered lattice in Figure 1(ii) resembles a sparser version of Figure 1(iii). The additional resonance is, therefore, just an SLR corresponding to the effective periodicity P_y' , with an additional resonant wavelength $\lambda_{\text{SLR}}' = nP_y'$. This is further supported by examining Figure 1(iii), which shows the corresponding transmission profile with $P_y' = 2P_y/3$. Hence, the altered lattice arrangement can be viewed as combinations between two different periodic lattice arrangements. Such bipartite array lattice systems^{26–29} have extensively been studied, and our numerical results are consistent with these studies.

We next examine the near-field profile of the metasurface. Figure 2a illustrates the x -polarized electric field of all three lattices shown in Figure 1. If we compare the electric field profile in Figure 2a (ii) with that of another perfect lattice arrangement with a periodicity of $2P_y/3$ at a wavelength of 1040 nm (Figure 2a (iii)), the same SLR modes are excited at the same wavelength. Hence, the additional SLR can be

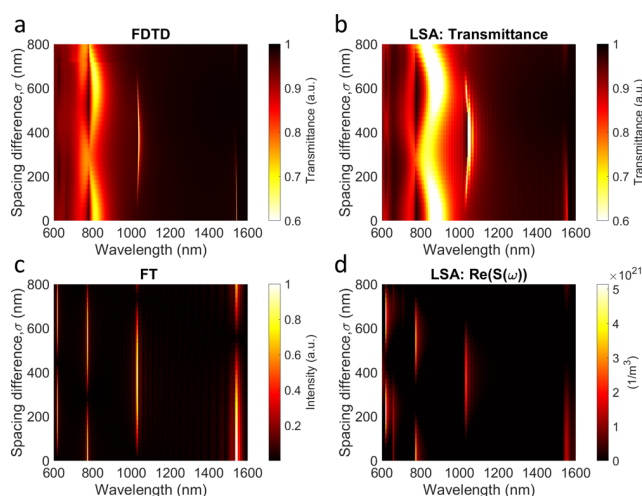


Figure 3. The evolution of the aperiodic SLR mode. (a) The FDTD-calculated transmission profiles with respects to the spacing difference σ . (b) LSA-simulated transmission spectra plotted as a function of σ . The calculated LSPR and SLR modes are largely consistent with the calculations in (a). (c) The FT-calculated power spectra with varying σ . (d) The LSA-simulated real part of lattice sum function, $\text{Re}(S(\omega))$, plotted as a function of σ . The spectral features are consistent with the FT calculations in (c).

regarded as an SLR mode with a periodicity of $2P_y/3$, but missing particles.

To observe the emergence of this SLR mode, we perform a series of FDTD simulations as a function of σ . We present the simulation results in Figure 3a. As shown in this figure, for $\sigma = 0$ nm, the new SLR does not appear at 1040 nm since the lattice arrangement is still rectangular. As σ gradually increases, the periodic SLR mode at 1550 nm starts to vanish due to the cancellation produced by the particle in the unit cell being located at the antinodes of the electric field with opposite sign, and a different SLR mode begins to appear when σ is changed from 80 to 640 nm at a wavelength of 1040 nm. The most pronounced resonance occurs when $\sigma \approx 354$ nm since this corresponds to approximately a period of $2P_y/3$.

We employ the lattice sum approach (LSA)^{30,31} to gain further insight into these metasurfaces. In this model, the effective polarizability induced in a single particle can be calculated by taking into account the change in the local field experienced by the particle due to the rescattered fields of the surrounding neighbor particles in the lattice. One of the main advantages of this method is that the computation time is much faster compared to a standard FDTD simulation with a superlattice element with periodic boundary conditions.^{11,12} On a standard desktop computer, the LSA simulations of a $150 \times 150 \mu\text{m}^2$ lattice for the 2790 antenna placements shown in Figure 3a took ~ 1 min for the entire spectral sweep (600–1600 nm), whereas the FDTD simulations of two-particle superlattices with periodic boundary condition took ~ 1 h. Clearly, the FDTD calculation of complete metasurfaces is computationally prohibitive. In this paper, we modify the lattice sum by including the effect of σ with a lattice size of $150 \times 150 \mu\text{m}^2$, and perform the corresponding calculations concerning σ , as illustrated in Figure 3b (see also Methods). By comparing this result with that shown in Figure 3a, we demonstrate that the transmission spectra obtained by LSA calculations are in excellent agreement with FDTD simulations

in terms of predicting the resonance wavelengths for the LSPR and SLR.

We are now ready to introduce the theory behind FLRs. The two SLRs in our example originate from the various periodicities present in the lattice (P_y and $2P_y/3$). Any discussions of periodicities naturally suggest the possibility of using Fourier series; indeed, we find that taking a Fourier transform (FT) of the particle locations may reveal the positions of the resonances. This idea is the essence of the design methodology of FLR metasurfaces. To demonstrate this idea by way of an example, we represent the lattice using the function $f(y)$; this function consists of a series of Gaussian profiles centered at the y -coordinates of individual nanoparticles, with a spacing corresponding to the periodicity of the actual lattice, P_y , between each profile (see Methods). We generate a series of different $f(y)$ functions for a range of values of σ ($\sigma = 0$ to 800 nm); these different $f(y)$ functions each represent a different lattice with increasing amounts of symmetry-breaking. We then take the FTs of each of these functions, and plot the resulting power spectra in Figure 3c. We compare this result to that of Figure 3d, which shows the LSA-simulated real part of lattice sum function, $\text{Re}(S(\omega))$, also as a function of σ (see eq 2). The resemblance between these two figures is evident upon inspection: the power spectrum (Figure 3c) in the FT calculation has peaks in the exact wavelengths where the $\text{Re}(S(\omega))$ calculation (Figure 3d) features the lattice resonances. This agreement indicates that these additional SLRs can be predicted with a simple FT of the perturbed lattices; we call this predictive design approach the Fourier lattice resonance (FLR) method. Although the SLRs for this particular lattice geometry can also be trivially explained using the Rayleigh Anomalies (RA),³² our model introduces an additional degree of freedom in designing metasurfaces. Given that the RA model depends on periodic structures, there are many lattice arrangements which it can not treat. We can therefore view our treatment, which can consider even aperiodic lattices, as a generalization of the RA model. The additional degree of freedom will be discussed in a subsequent section.

Experimental Verifications of FLRs. To experimentally verify the FLR model, we fabricated two sets of metasurfaces consisting of rectangular nanoparticles. In Figure 4a, the images of the devices are presented; each subfigure in Figure 4a represents the actual device with different values of σ , and with a P_y of 1063 nm. This set of metasurfaces has nanoparticle dimensions of $L_x = 110$ nm and $L_y = 180$ nm, and lattice sizes of $150 \times 150 \mu\text{m}^2$. The calculated transmission spectra for these devices are shown in Figure 4b and are in good agreement with the experimental data in Figure 4c. The experimental setup and procedure are described in the Methods. As predicted, the periodic SLR mode at 1040 nm vanishes as σ decreases. Furthermore, a new SLR starts arising when $\sigma = 88$ nm, and is most prominent when $\sigma = 354$ nm, which agrees with the LSA and the FDTD simulations, supporting our theoretical interpretation. Notably, the Q -factors of this set of devices range from 80 to 90, and the sharpest aperiodic SLR dip has a Q -factor of 90 with $P_y = 1063$ nm and $\sigma = 354$ nm.

Our model also works with different values of P_y . Here, we fabricated another set of metasurfaces with $P_y = 1598$ nm (Figure 4d) and the same nanoparticle sizes as the first set of the devices. Similarly to the first set of metasurfaces, the simulated transmission profiles of the second set of

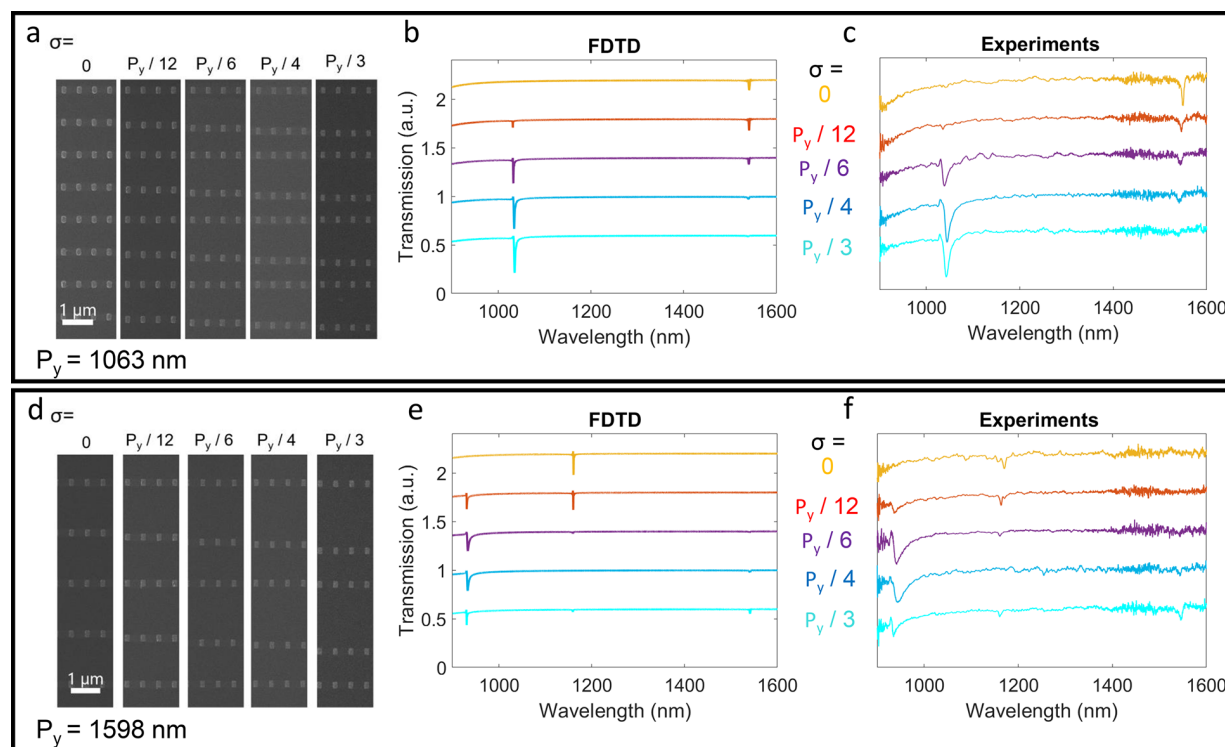


Figure 4. Experimental observation of metasurfaces with multiple SLR modes. (a,d) Helium ion microscopic images of the fabricated metasurfaces prior to cladding deposition. Each subfigure corresponds to an image with a different σ . For (a), all metasurfaces have $P_y = 1063$ nm, whereas for the metasurfaces in (d), $P_y = 1598$ nm. (b,e) The simulated transmittance of the corresponding metasurfaces with (b) $P_y = 1063$ nm and (e) $P_y = 1598$ nm. (c,f) The measured transmission spectra of the metasurfaces with (c) $P_y = 1063$ nm and (f) $P_y = 1598$ nm.

metasurfaces ($P_y = 1598$ nm) in Figure 4e are also in good agreement with the experimental data (Figure 4f), where a new SLR mode for this system is predicted to occur at 1550 nm and $\sigma = 354$ nm. Despite the extinction coefficients of the resonances in these metasurfaces being smaller than the first set, the Q -factors of these devices are relatively higher. The Q -factors range from 170 to 220, where the lattice resonance with the highest Q -factor appears at 1150 nm and $\sigma = 532$ nm. In the first set of devices, the spectral distance between the SLR at 1550 nm and the second SLR in our spectrum was 504 nm, in the second set, the distance is only 381 nm. This hints at the flexibility of modulated lattices to place SLRs at flexibly spectral locations.

We have just shown that the LSA succeeds at describing the transmission spectra of a modified lattice arrangement. However, a discrepancy arises in the Q -factor predicted by this method when compared to FDTD simulations and the experimental results, which we attribute to the difference in array size.^{33,34} Because the nanoparticle density in the second set of metasurfaces is smaller although the array size is the same, the extinction ratio and Q -factor are lower than in the first set, making the second set of metasurfaces harder to characterize.

Reverse-Engineering of FLRs. Since the properties of the SLRs in bipartite lattices can be predicted by using the FLR method, in principle, the process can be reverse-engineered: one could begin with the desired transmission profile, then use the FT of that spectrum to directly engineer the nanoparticle placement to generate the desired spectrum. To demonstrate this idea, we first select a set of desired resonance wavelengths and create a virtual spectrum (Figure 5a), where we are

deliberately placing two SLRs at 1150 and 1220 nm. We also include replicas of these two desired resonances represented as integer N th harmonics in this virtual spectrum because there will naturally appear higher-order diffraction terms at $\lambda_{\text{SLR}}/2$, $\lambda_{\text{SLR}}/3$, etc for any lattice resonance (see Methods). Thus, the FT-simulated transmission profile of a lattice must reproduce these corresponding features. We then take the inverse FT (IFT) of the virtual spectrum (Figure 5a), which is shown in Figure 5b. Furthermore, we acquired the corresponding particle locations using a peak-finder function in Figure 5b and calculated the transmission spectra of the IFT-generated lattice arrangement using LSA with the obtained particle locations (see also Methods for more details). We observe that the corresponding SLR modes for each set are induced at the desired wavelengths (Figure 5d).

Experimental Demonstration of Reverse-Engineered FLRs. To experimentally demonstrate the reverse-engineering capabilities of the FLR method, we fabricate two devices with different sets of resonance wavelengths, one with resonances at $\lambda = 1150$ and 1220 nm (FLR1) and another, equivalent lattice prepared for resonances at $\lambda = 1310$ and 1550 nm (FLR2), where the array size is $100 \times 400 \mu\text{m}^2$ for both devices. Figure 5c shows images of subsets of the lattices for the FLR1 and FLR2 metasurfaces. After performing the measurements on these devices, we compare the LSA simulations (Figure 5d) with the experimental data (Figure 5e). The predicted resonance wavelengths from the LSA simulations are in good agreement with the experimental results of both devices. This agreement suggests that this method can be used to design resonance wavelengths flexibly. We also experimentally measured the Q -factors for these lattice resonances for both

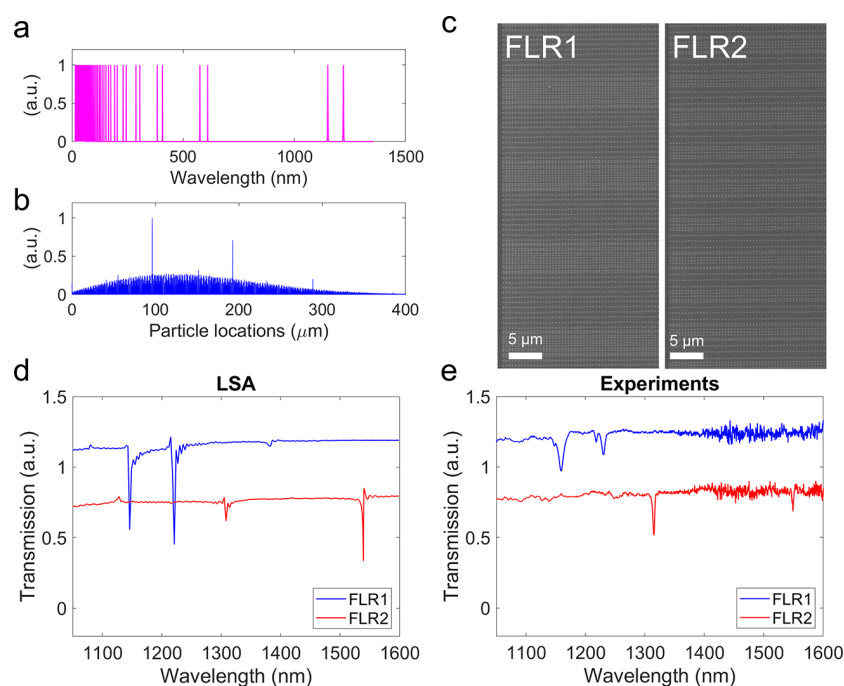


Figure 5. The FLR metasurface. (a) The generated virtual spectrum. We created a spectrum with resonance wavelengths of 1150 and 1220 nm, including their corresponding harmonics since each lattice resonance will naturally generate higher-order diffraction terms. The vertical axis of the figure is the virtual beam intensity, which we set to unity. (b) The IFT of the virtual spectrum. The x -axis of the diagram indicates the corresponding particle locations for the desired wavelength combination. The vertical axis of the figure is IFT power spectrum intensity; we employ a peak-finder function with a small threshold (0.015) to determine the particle locations. The superlattice for FLR1 is nonrepeating over ~ 20 antenna in y -axis (here equivalent to $\sim 6 \mu\text{m}^2$), making FDTD simulation of this device prohibitive, but still possible with LSA. (c) SEM images of subsets of the lattices for FLR1 and FLR2 metasurfaces. (d) Calculated transmission spectra of the FLR metasurfaces using LSA method. The SLRs arise at the desired wavelengths. (e) The measured transmission spectra of the corresponding FLR metasurfaces.

samples. The experimental Q -factors of the lattice resonances in the FLR1 metasurface are 130 at $\lambda = 1150$ nm and 200 at 1220 nm, and the experimental Q -factors for the FLR2 metasurface are 400 at $\lambda = 1310$ nm and 800 at 1550 nm. Fabricating the same device with a larger array size would likely increase the depth and Q -factor of the resonances.^{11,12,34} These agreements also imply that the LSA model can be used for calculations of aperiodic lattice array.^{9,11,12}

The highest Q -factor of these FLRs is 800 (FLR2, at a wavelength of 1550 nm), which is 2 orders of magnitude higher than those associated with the LSPRs of the individual nanoparticles and an order of magnitude higher than that of Fabry–Pérot SLR modes.¹² With such high Q -factors and the strong optical nonlinearity of metals,³⁵ the FLR metasurfaces could find applications in nonlinear processes, such as nondegenerate four-wave mixing (FWM).³⁶

To consider how existing approaches could be complemented by our FLR method, we consider a few recent, key examples from the literature: a recent work showed that a single dielectric nanoparticle could be engineered to have multiple resonances, some of which showed Q -factors ~ 190 .³⁷ This required careful simulation of the nanoparticle dimensions and precise fabrication. By comparison, our FLR method could likely design a metasurface with similar multiple resonances from the spectrum itself. Obviously the nature of the resonators themselves are very different, but this exemplifies the ease of our design approach. Other related attempts in generating multiple resonances such as inducing Fabry–Pérot SLRs using a cladding,¹² and using orthogonal polarizations^{38,39} in the lattice are often restricted to

resonances that are periodic in frequency. Our method is not restricted to periodic resonances, and it only assumes dipole effects of the particles, leading to more straightforward computations.

Designing the FLR metasurface using standard FDTD simulations would be exceptionally challenging because the lack of symmetry in the lattice eliminates the possibility of simulating a small supercell, and the computational time increases with the size of the lattice arrangement.⁴⁰ In contrast, the computational time required by the FLR method is reasonable (typically within 3 min), necessitating the computation of only a single FT per lattice.

Other recent work has computed FTs to determine the 3D structure of a surface for applications in optical wavefront shaping; thus, fabricating such structure requires more sophisticated techniques.^{14,41} By contrast, our work aims to find a desired transmission spectrum, and our method only utilizes standard electron-beam lithography techniques instead of 3D structures, which leads to a more straightforward fabrication.

Other related work has extensively demonstrated designing multilayer thin film stacks using FTs for applications in optical filtering.⁴² Noting the similarity of our work to the study of ref.,⁴² we believe that our methodology could be further extended to 3D lattices by combining our design method with the developed analytical method.

Future work on this platform could look into modifying the nanoparticle geometries to tune the width and depth of the individual resonances. Furthermore, we only took the position of the particle locations and ignored the magnitude of the

peaks in the power spectrum when performing the IFTs. Some information is encoded in these magnitudes on the scattering amplitude of individual nanoparticles in the array. This information could perhaps be incorporated in future metasurfaces to modulate the individual extinction ratio of each resonance. Moreover, other more complex systems can be examined using our method, but are left for future studies. For example, the system could consist of arrays with complex unit cells in which the particles are placed at positions with arbitrary x - and y -coordinates, or we could consider excitation at an oblique incidence, or with the polarization not aligned to one of the array axes.

The Q -factor of the FLRs can be increased further by using dielectric particles. However, in those cases, higher-order multipoles would need to be taken into consideration.³⁷ In this work, we did not modify the arrangement of the particles in the x -direction. We note that such modifications should give rise to a different set of resonances that could be excited by using orthogonal polarization, that is, y -polarized light.³⁸ One possible application would be to modify the LSA calculations to generate orbital angular momentum (OAM) modes by introducing particle size disorders or different particle geometries.

CONCLUSIONS

We have theoretically proposed and experimentally demonstrated the concept of FLRs. The fabricated devices in this paper enable SLRs at multiple simultaneous wavelengths, and the experimental results are in good agreement with our FLR calculations. Additionally, these devices require only a standard fabrication procedure, and they can be easily expanded upon to generate multiple resonances that can be placed nearly flexibly within a spectral octave. From a broader perspective, this method is possible because we exploit a previously ignored degree of freedom by breaking the lattice periodicity, and this modeling is only possible thanks to large-scale modeling techniques like LSA. We anticipate that this design method will become significant in realizing resonant metasurfaces for many optical applications.

METHODS

Simulation. FDTD Simulations. A commercial three-dimensional finite-difference time-domain (FDTD) software package is utilized to perform full-wave simulations for single rectangular nanoparticles, periodic metasurfaces, and modulated metasurfaces. For the single nanoparticle simulations, the total-field scattered-field (TFSF) method is used to extract the single particle polarizability in all three dimensions: α_{xx} , α_{yy} , and α_{zz} .⁴³ For the periodic and modulated metasurfaces, a single unit cell was simulated using periodic boundary conditions in the in-plane dimensions and perfectly matched layers in the out-of-plane dimension. All three cases were modeled using fully dispersive optical material properties for silica and for gold.⁴⁴ Minimal artificial absorption ($\text{Im}(n) \approx 10^{-4}$) was added to the background medium to reduce numerical divergences.

Lattice Sum Approach. The lattice sum approach (LSA) is a simplified version of the discrete-dipole approximation (DDA) method.^{30,31} The main difference between these two methods is that the LSA assumes that the dipole moments of all interacting nanoparticles are identical. Thus, the dipole moment of any nanoparticle can be simplified as

$$\mathbf{p} = \frac{\epsilon_0 \alpha(\omega) \mathbf{E}_{\text{inc}}}{1 - \epsilon_0 \alpha(\omega) S(\omega)} \equiv \epsilon_0 \alpha^*(\omega) \mathbf{E}_{\text{inc}} \quad (1)$$

where the effect of interparticle coupling is incorporated in the lattice sum $S(\omega)$, $\alpha^*(\omega)$ is the effective polarizability, and $\alpha(\omega)$ is the single nanoparticle polarizability obtained from the TFSF method. The $S(\omega)$ can be written as

$$S(\omega) = \sum_{j=1}^N \frac{\exp(ikr_j)}{\epsilon_0 r_j} \left[k^2 + \frac{(1 - ikr_j)(3\cos^2 \theta_j - 1)}{r_j^2} \right] \quad (2)$$

where r_j is the spacing to the j th dipole, k is the wavenumber, and θ_j is the angle between r_j . For a periodic metasurface, r_j is just the periodicity P_v multiplied by j and the indices v indicates the x - or y -axis.

Fourier Transform of the Function $f(y)$. The function $f(y)$ that mimics the lattice arrangement is considered by producing a series of Gaussian profiles. Each Gaussian profile represents a nanoparticle, and the Gaussian peak intensity is set to 1. We set the bandwidths of these Gaussian profiles to be significantly smaller than the spacing between the particles (bandwidth-to-spacing ratio is ~ 100); thus, we can assume that the particles act like point-like dipoles under the applied incident field, similar to the assumption made in the LSA model. Next, the spacing between each Gaussian profile is P_y in the periodic case. When we considered a modulated lattice arrangement, the position of every second nanoparticle was shifted by σ . Then, we performed FT of the function with respects to y -axis, and we obtained the density plot in Figure 3c.

Combining LSA and IFT Calculations. We generate a function $f(y)$ as explained in the main text and previous subsection. This function contains a series of Gaussian peaks: two of them are placed at the desired resonance wavelengths (e.g., 1150 and 1220 nm); the remaining ones are placed at the integer harmonics for each resonance (e.g., 575 nm, 383.3 nm, 287.5 nm, ...and 610 nm, 406.7 nm, 305 nm, ..., respectively). These resonances correspond to the Rayleigh anomalies (RA) for $m = 0$:

$$\lambda \sim \frac{n}{\sqrt{\left(\frac{j}{P_y}\right)^2 + \left(\frac{m}{P_x}\right)^2}}, \quad (3)$$

where n is the refractive index, and j and m are the RA orders along the y - and x -axis, respectively. As we only consider $m = 0$ cases to simplify our model, only x -polarized beams are taken into account and P_y makes the only contribution to the system. All profiles have the same intensity, and the full width at half-maximum (fwhm) of the profiles are significantly smaller than their separation (the fwhm-to-spacing ratio is ~ 100). Hence, we obtain the plot shown in Figure 5a.

We then perform an IFT of $f(y)$ (Figure 5b). The x -axis is inverted so that we are plotting against units of length instead of inverse-length. We identify the locations of the peaks in Figure 5b using a peak-finder function. The resulting list of locations correspond to the locations of the centers of the nanoparticles needed to generate the spectrum in Figure 5a.

To avoid overlap between neighboring particles, and to ensure the possibility of nanofabrication, we enforce a minimum distance between the centers of nanoparticles, here set to 250 nm. We also truncate the total number of particles at the ends of the arrays to obtain a desired array size, here 400 μm .

To determine the transmission spectra of the IFT-simulated lattice arrangement, we insert the calculated particle locations (Figure 5b) into r_j in the y -axis in eq 1. We obtain the corresponding effective $S(\omega)$ which we use to calculate α^* to determine the effective dipole moment using eq 2. We finally use α^* to obtain the transmission spectra shown in Figure 5d.

Fabrication. The metasurfaces are fabricated using a standard metal lift-off process and a positive-tone resist bilayer. We started with a fused silica substrate and defined the pattern using electron-beam lithography with the help of a commercial conductive polymer. The mask was designed using shape correction proximity error correction⁴⁵ to compensate for corner rounding. Following the development, gold was deposited using thermal evaporation. The final silica cladding layer was deposited using sputtering. The backside of

the silica substrate was coated with an antireflective coating to minimize substrate-related etalon fringes.

Experimental Setup. A collimated broadband supercontinuum laser source was used to illuminate the devices with a wavelength spectrum ranging from 470 to 2400 nm. We used a linear polarizing optical filter to control the light beam polarization. Then, the light beam was transmitted through the device and a lens imaged the sample onto the detector array. We placed a pinhole with a diameter of 100 μm in the image plane to choose the desired metasurface. After that, the remaining light beam was guided into a multimode fiber with a diameter of 400 μm , which was coupled into an optical spectrum analyzer. Finally, we normalized the transmission spectrum of the light beam to a background trace of the substrate without gold nanostructures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.1c10710>.

Multiple simulated transmission profiles for a series of FLR metasurfaces with different combinations of arbitrarily selected resonance wavelengths have been demonstrated (PDF)

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Author Contributions

T.L. and O.R. conceived the basic idea for this work. T.L. and Y.V. conducted the transmission measurements. T.L., O.R., and M.S.B.A. designed the experiment. R.A. and L.C.

calculated single particle's polarizability. T.L. and O.R. carried out the simulations. O.R. fabricated the devices. T.L., O.R., Y.V., and J.U. analyzed the experimental results. R.W.B., J.U., M.J.H., and K.D. supervised the research and the development of the manuscript. T.L. and O.R. wrote the first draft of the manuscript, and all authors subsequently took part in the revision process and approved the final copy of the manuscript.

Notes

The authors declare no competing financial interest.

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Supporting information for Fourier-Engineered Plasmonic Lattice Resonances

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Below is the supplementary information for Fourier-Engineered Plasmonic Lattice Resonances by Theng-Loo Lim, Yaswant Vaddi, M. Saad Bin-Alam, Lin Cheng, Rasoul Alaei, Jeremy Upham, Mikko J. Huttunen, Ksenia Dolgaleva, Orad Reshef, and Robert W. Boyd. It contains one section, in which we demonstrate multiple simulated transmission profiles for a series of FLR metasurfaces with different combinations of arbitrarily-selected resonance wavelengths.

Different combinations of selected wavelengths

In this section, we use the LSA to simulate FLR metasurfaces with several different combinations of selected wavelengths. These metasurfaces all consist of arrays of gold nanoparticles dimensions of 110 by 180 nm². These simulations prove the flexibility of the FLR method to design a variety of transmission profiles.

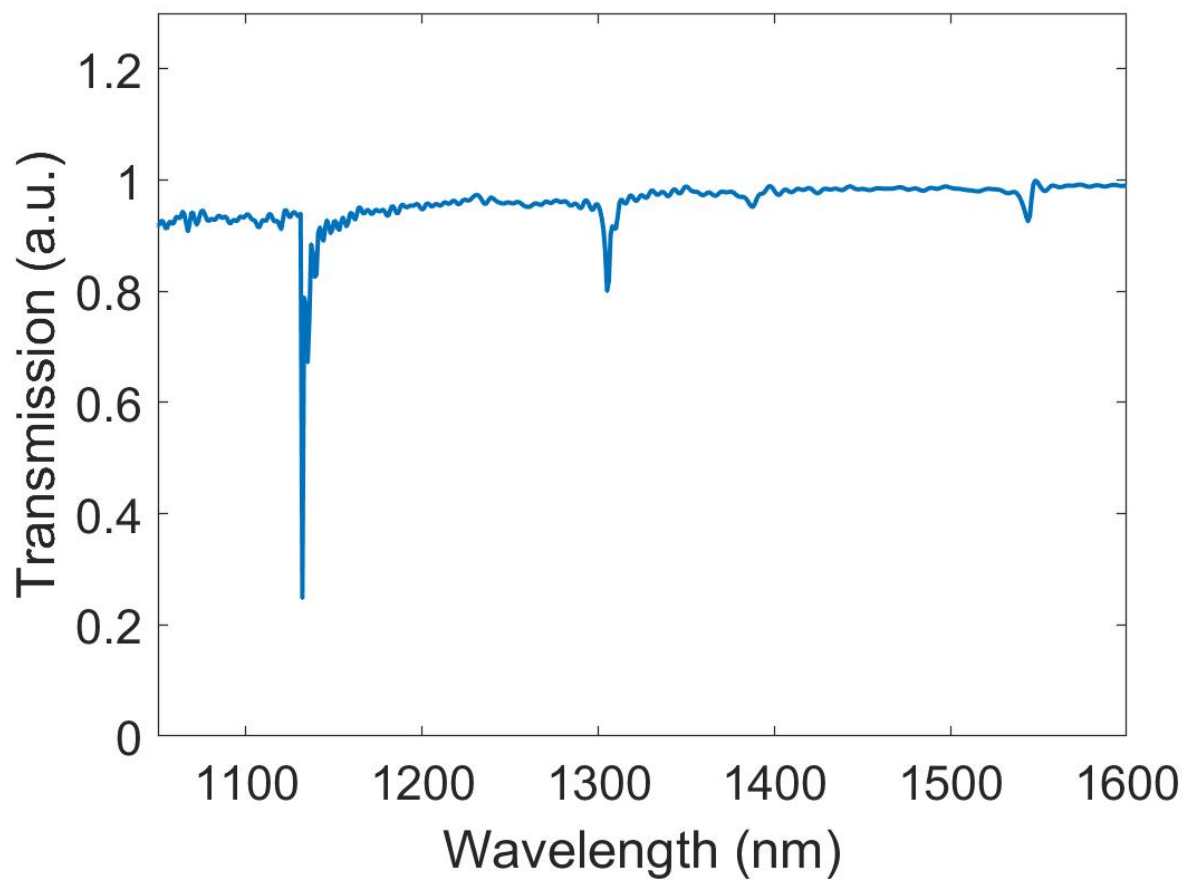


Figure 1: The selected wavelengths are 1134 nm, 1310 nm, and 1555 nm.

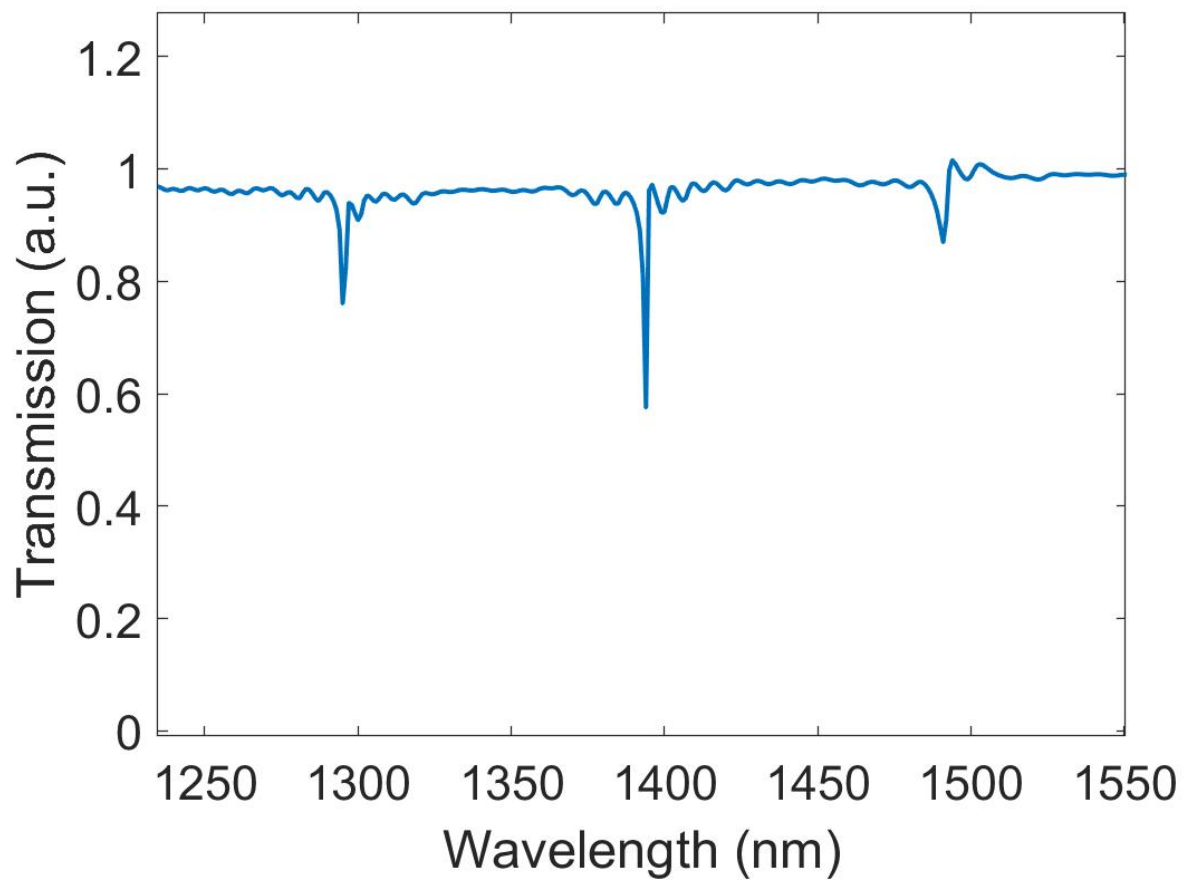


Figure 2: The selected wavelengths are 1300 nm, 1400 nm, and 1500 nm.

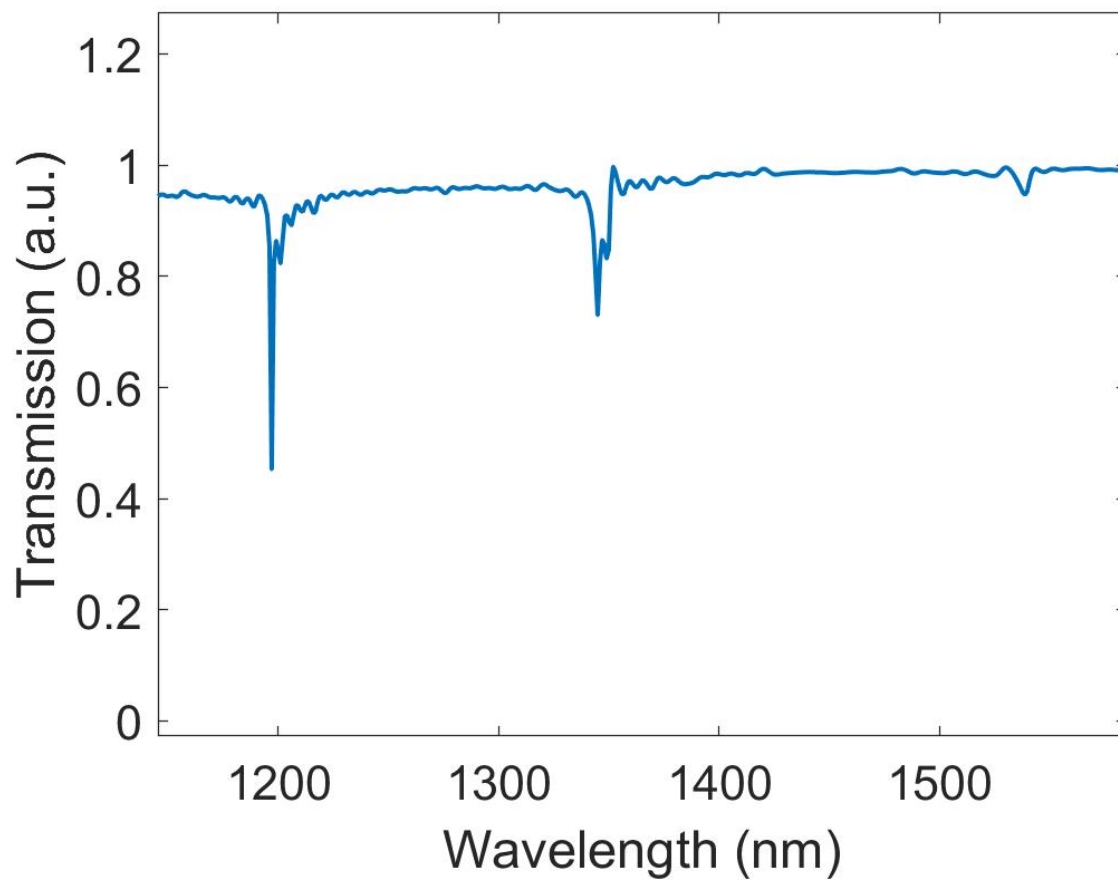


Figure 3: The selected wavelengths are 1200 nm, 1350 nm, and 1550 nm.

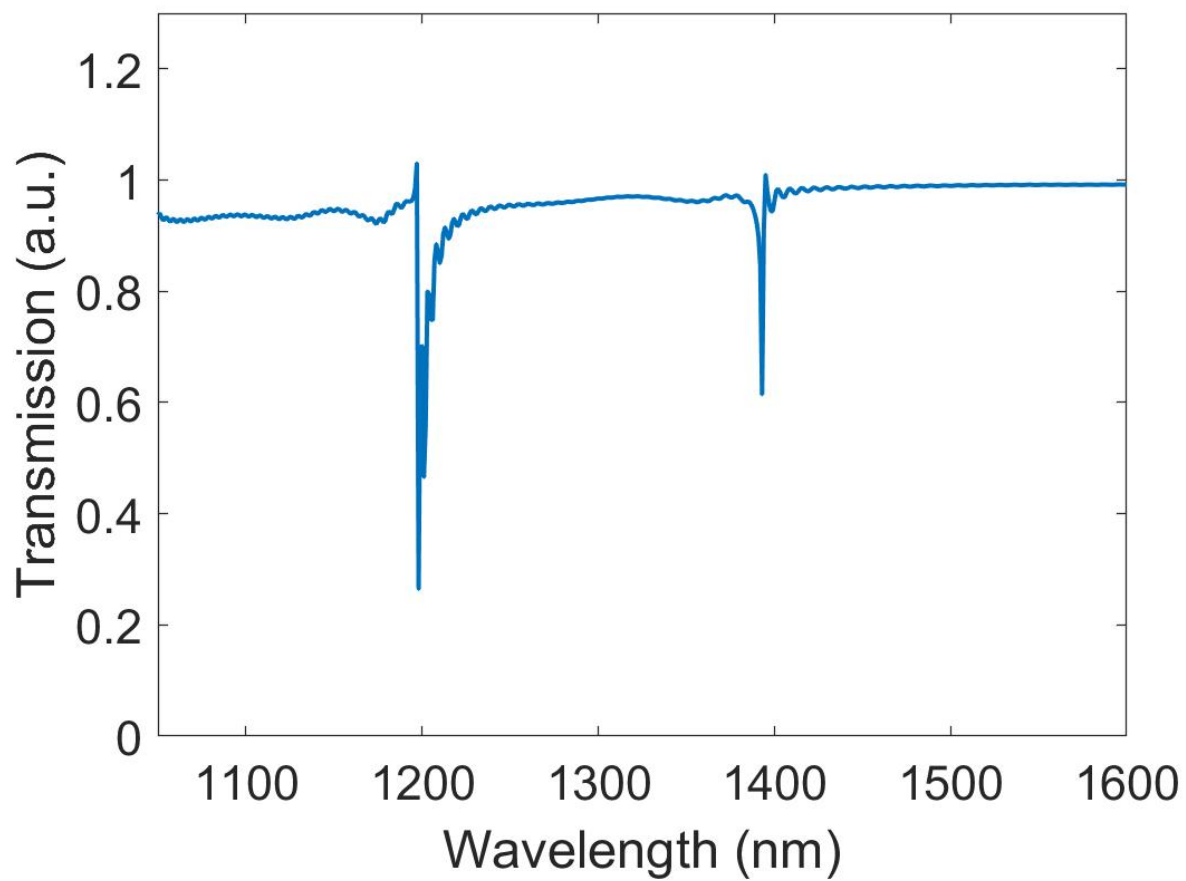


Figure 4: The selected wavelengths are 1200 nm, and 1400 nm.

Appendix B

Interactions of fundamental mie modes with thin epsilon-near-zero substrates

Contribution Statement

This work was conceived by Dr. Mohammad Karimi and Dr. Zahirul Alam. The metasurface design and fabrication were carried out by Dr. Mohammad Karimi and Dr. Kashif Masud Awan. The study investigates the strong coupling between electric and magnetic dipole resonances of dielectric nanoantennas and the ENZ mode of an ITO substrate, supported by analytical, numerical, and experimental results.

My involvement in this project focused on the experimental characterization of the fabricated samples. I performed linear optical measurements of the metasurfaces in collaboration with Dr. Mohammad Karimi. In addition, I independently constructed the nonlinear pump-probe experimental setup used to measure the nonlinear change in the structure's transmission.

My contributions to the work are summarized below:

1. Performing linear optical characterization of the metasurface samples (contributor, alongside Dr. Mohammad Karimi).
2. Designing and building the nonlinear pump–probe experimental setup (primary contributor).

Interactions of Fundamental Mie Modes with Thin Epsilon-near-Zero Substrates

Mohammad Karimi,^{*} Kashif Masud Awan, Yaswant Vaddi, Rasoul Alaei, Jeremy Upham, M. Zahirul Alam,^{*} and Robert W. Boyd



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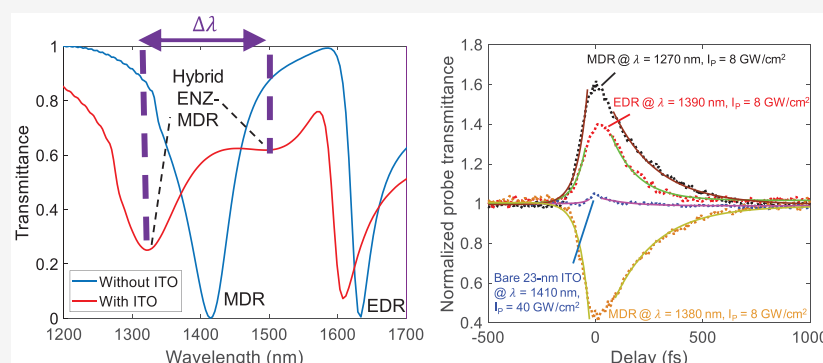
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Supporting Information



ABSTRACT: Extensive research has focused on Mie modes in dielectric nanoresonators, enabling the creation of thin optical devices surpassing their bulk counterparts. This study investigates the interactions between two fundamental Mie modes, electric and magnetic dipoles, and the epsilon-near-zero (ENZ) mode. Analytical, simulation, and experimental analyses reveal that the presence of the ENZ substrate significantly modifies these modes despite a large size mismatch. Electric and magnetic dipole modes, both with ~ 12 THz line widths, exhibit 21 and 26 THz anticrossings, respectively, when coupled to the ENZ mode, indicating strong coupling. We also demonstrate that this strongly coupled system yields notably large subpicosecond nonlinear responses. Our results establish a solid foundation for designing functional, nonlinear, dynamic dielectric metasurfaces with ENZ materials.

KEYWORDS: Nonlinear Optics, Epsilon-near-Zero, Metasurface, Nano-optics

Dielectric nanoantennas, constructed from materials with high refractive indices and low loss compared to plasmonic counterparts, serve as the building blocks for the next generation of nanophotonic devices.¹ Unlike plasmonic nanoantennas, they easily integrate into existing CMOS fabrication lines² and, even with simple geometries, support multiple optical resonances, including electric and magnetic dipoles and quadrupoles, referred to as Mie modes.³ The availability of multiple resonant modes in the dielectric nanoantennas allows for tailoring near-field and far-field properties of light.^{4–22} In a parallel vein, thin layers of ENZ materials have distinctive linear and nonlinear optical properties arising from a nearly zero real part of permittivity within specific wavelength ranges.²³ Notably, materials such as indium tin oxide (ITO) and aluminum-doped zinc oxide (AZO) have been extensively explored for their large nonlinear responses.^{24,25}

In this work, we investigate how the Mie resonances of the dielectric nanoantenna couple with the ENZ mode of a thin ITO substrate. An ENZ mode is an inherently dark mode with a largely enhanced electric field inside a very thin ENZ layer

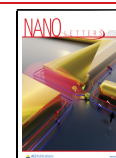
sandwiched between two dielectrics.²⁶ Extensive research has been conducted on the interaction between the modes of plasmonic nanostructures and the ENZ mode of various near-zero-permittivity materials, including transparent conducting oxides,^{27,28} semiconductors,²⁹ and phonon-based ENZ materials.³⁰ Plasmonic systems often exhibit pronounced losses, which need to be addressed. Additionally, achieving higher-order modes in these systems necessitates intricate engineering efforts to shape the antennas, adding an additional layer of complexity to the design process.³¹ In Mie resonances, unlike plasmonic resonances, the mode is typically concentrated within the dielectric material rather than along the surfaces; therefore, the opportunity for strong modal overlap with the ENZ mode of a nearby structure is expected to be smaller.

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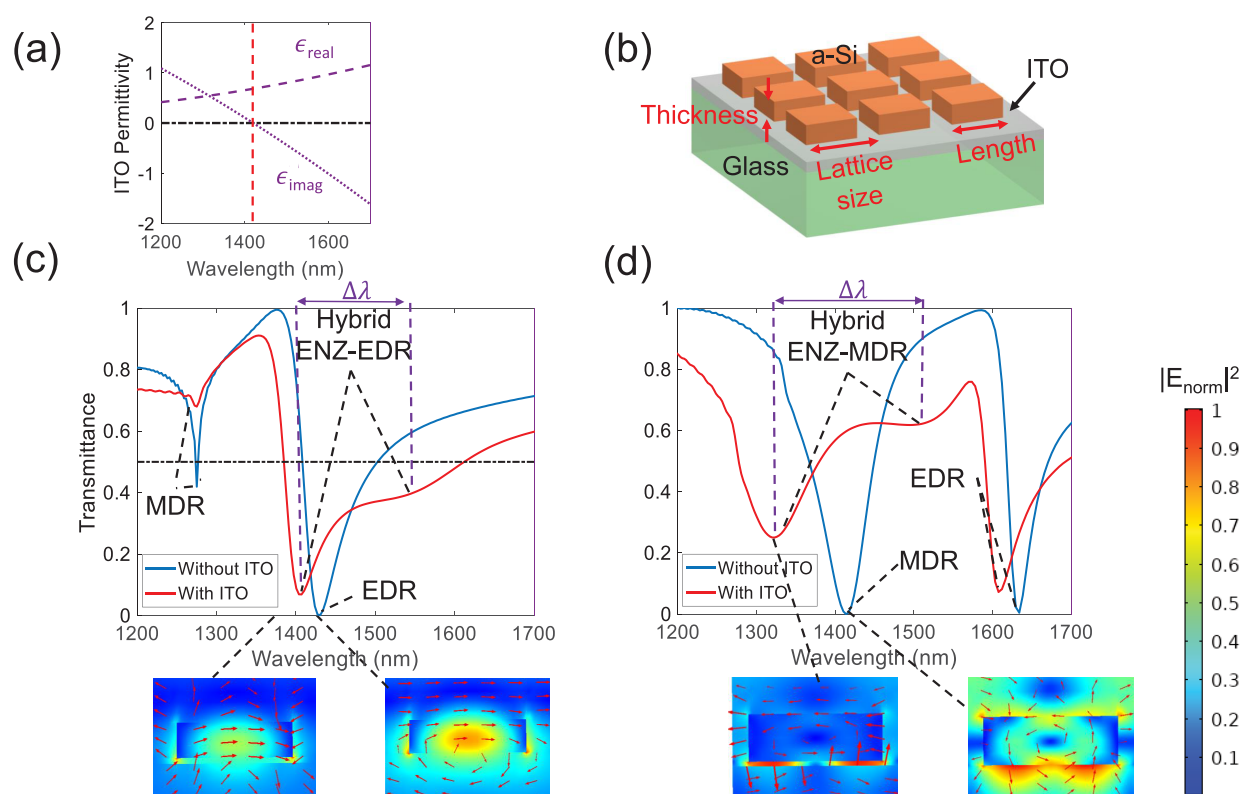


Figure 1. (a) The real and imaginary parts of the permittivity of the ITO sample taken from the ellipsometry data; the red dashed line specifies that 1410 nm is the zero crossing point. (b) The schematics of the a-Si metasurface on ITO on glass. (c, d) Comparison of the transmittance of the metasurfaces over the glass and over ITO for observing the interaction of the (c) electric dipole resonance (EDR) and (d) magnetic dipole resonance (MDR) with the ENZ mode. The length, width, and thickness of the antennas and the lattice constant in the figure are 560, 500, 140, and 850 nm, respectively, for part c and 650, 650, 210, and 810 nm, respectively, for part d. The parameter $\Delta\lambda$ indicates the amount of anticrossing that occurs due to the strong coupling effect, and it is around 140 nm for the EDR case and around 200 nm for the MDR case. The insets show the electric field amplitude distribution and direction around the antennas for the different resonance modes specified in the transmittance plots.

However, we show that even for a simple dielectric nanoantenna geometry, the field enhancement of Mie modes is sufficient to achieve strong coupling with the ENZ mode. We experimentally and theoretically demonstrate that the two fundamental Mie modes (electric and magnetic dipole resonances) of silicon dielectric antennas can strongly couple with the ENZ mode of a 23 nm-thick ITO substrate. Furthermore, using simple pump–probe measurements, we demonstrate strongly enhanced transmission modulation of these structures in comparison to bare ITO. This suggests that the metasurface composed of dielectric nanoantennas and ENZ thin films has significant potential for nonlinear optical applications, at least as significant and perhaps more varied than their plasmonic counterparts.

In general, the resonance wavelength of a Mie mode is a complicated function of the geometric and material properties of the dielectric nanoantenna. We selected cuboid antenna shapes since the three geometric parameters length, width, and height allow sufficient freedom to investigate the interaction between one fundamental dipole resonance (either electric or magnetic) and the ENZ mode while keeping the other dipole resonance spectrally separate from the ENZ resonance condition.³² Figures 1a and b demonstrate the permittivity of the ITO substrate we used and a schematic of the device with and without ITO, respectively. The ENZ mode resonance, as discussed in section 1 of the Supporting Information, is near the wavelength where the real part of the permittivity crosses

from positive to negative, that is, the wavelength at which Mie resonances could couple to the ENZ mode. In this work, we focus on the electric dipole resonance (EDR) and the magnetic dipole resonance (MDR) of the antennas. Higher-order modes, such as quadrupole, likely respond similarly but will be the subject of subsequent research. We designed two groups of metasurfaces, each specifically engineered to align either the EDR or the MDR with the wavelength of the ENZ mode, while ensuring all other resonance modes remain at least two line widths distant from the ENZ wavelength. To design the metasurfaces, we swept over different dimensions of the single antennas and the lattice constant over the glass in our simulations using Comsol Multiphysics while tracking the resonance wavelength and mode of each of the Mie resonances. We then found the dimensions that set the resonances to the ENZ mode's central wavelength, added the ITO layer as the substrate, and compared the results in the presence and absence of ITO. Figure 1 demonstrates the effect of a 23 nm layer of ITO as the substrate on the transmittance of one of our EDR samples and one of our MDR samples, respectively. The length, width, and thickness of the antennas and the lattice constant in Figure 1 are 560, 500, 140, and 850 nm, respectively, for the EDR case and 650, 650, 210, and 810 nm, respectively, for the MDR case. In both cases, the presence of ITO splits the Mie resonance into two hybrid modes: one at a shorter wavelength and one at a longer wavelength than the resonance wavelength of the same metasurfaces on glass; we

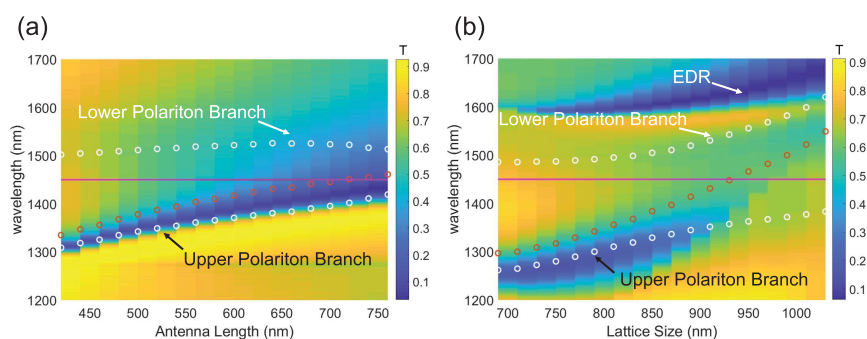


Figure 2. Comparison of analytical derivation and numerical simulation of hybridized mode splitting. To show tuning of (a) the EDR and (b) the MDR across the ENZ mode, transmittance spectra for different antenna lengths or lattice sizes, respectively, were simulated in Comsol Multiphysics. The red circles are the position of the EDR and MDR in parts a and b, respectively, with the antennas without ITO derived from the simulation results. The white circles indicate the positions of the upper and lower polariton branches predicted by the analytical solution.

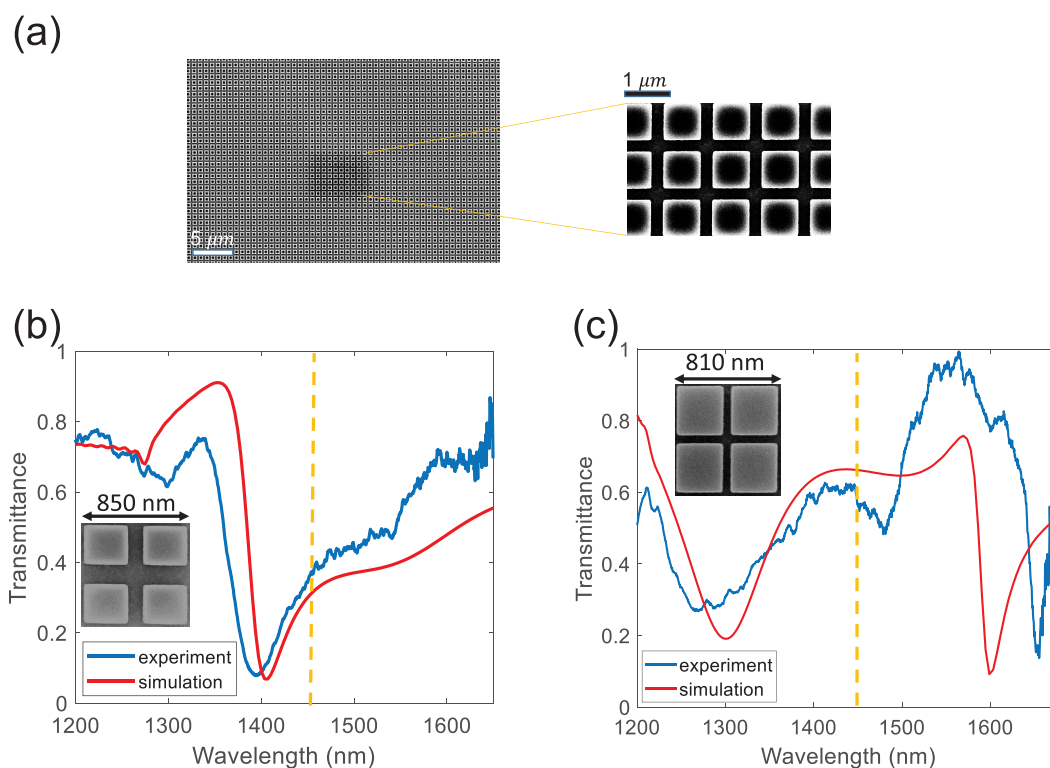


Figure 3. (a) SEM image of one of the fabricated devices. (b, c) Comparison of the transmittance in simulation and experiment of one representative EDR sample (b) and one representative MDR sample (c). The vertical dashed line shows the central wavelength of the ENZ mode. The SEM images in the insets show 4 unit cells of the metasurface for which the experimental data is shown. The dimensions of the samples were the same as those used in Figure 1. The orange dashed lines specify the central wavelength of the ENZ mode derived by solving the wave equation as explained in the Supporting Information.

call them the lower polariton branch and the upper polariton branch, respectively, for the remainder of the manuscript. Note that the lower polariton branch exhibits a smaller dip in transmittance than the upper polariton branch, which can be attributed to the non-negligible loss of ITO. A similar asymmetry in the depth of the transmission resonances has been reported before.^{33,34} The appearance of these hybrid modes is the main sign of coupling between the fundamental Mie modes and the ENZ mode.³⁵ The spectral separation of the hybrid modes, $\Delta\lambda$, is proportional to the strength of coupling, and the system is said to be in a strong coupling regime if the spectral separation is larger than the line width of the fundamental Mie mode in the absence of ITO.³⁵ These simulations predict hybridized mode splitting larger than the

FWHM line width of the Mie resonances without the ITO substrate, suggesting that the systems are in strong coupling regimes.

The field distributions of the EDR and MDR are distinguishable inside and in the vicinity of the nanoantennas at the resonance wavelength.^{32,36} The insets in Figure 1c and d show the electric field intensities and vectorial distributions at the EDR and MDR without the ITO thin film as well as the higher polariton branch of each when this ENZ substrate is included. At the EDR, the electric field concentrates within the center of the nanoantenna, with the polarization determined by the incident field. At the MDR, the electric field vectors circle inside the antenna such that the curl of the electric field points in the direction of the magnetic dipole. When introducing a

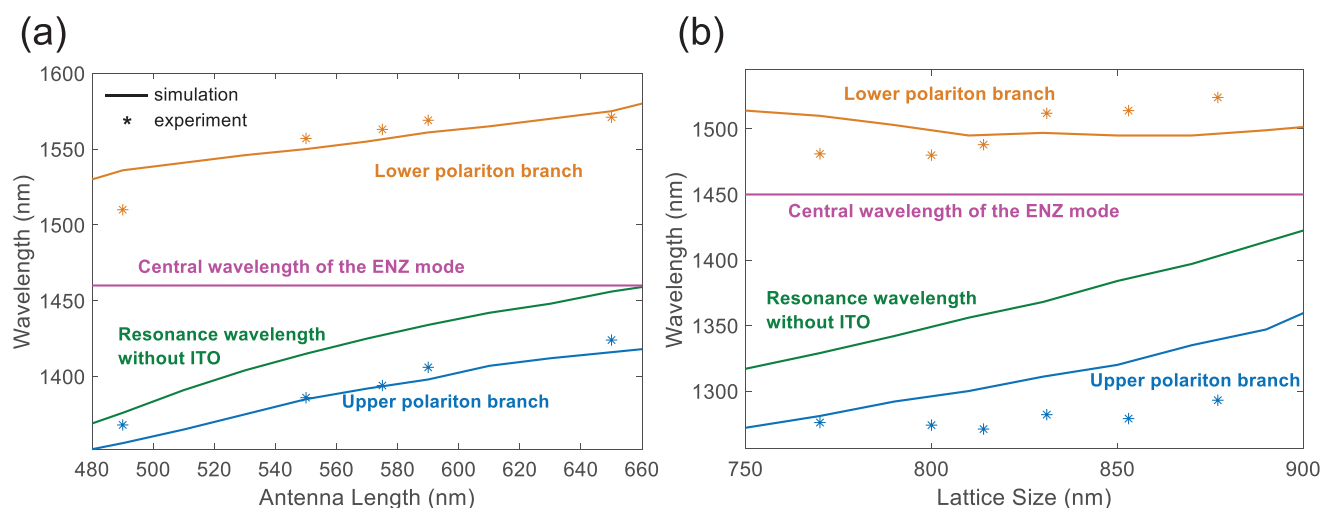


Figure 4. Positions of different resonances in the wavelength domain for (a) the EDR sample for different antenna lengths and (b) the MDR sample for different lattice sizes.

thin ITO layer as the substrate, the upper polariton resonances show that a visibly significant portion of the electric field within the antennas penetrates the ITO layer due to strong coupling for both resonances.

To investigate the strongly coupled system in more detail, we simulated the transmittance of the metasurfaces with different dimensions for the EDR and MDR samples using Comsol Multiphysics. Sweeping the dimensions such that one Mie resonance crossed the ENZ mode revealed the anticrossing of the hybridized modes in the transmittance. Figures 2a and b show the simulated transmittance at different wavelengths for EDR and MDR samples, respectively, as functions of the length of the antennas for the EDR samples and the size of the lattice for the MDR samples. The red circles in both figures specify the spectral positions of the numerically obtained resonances under study with metasurfaces over the glass without ITO, while the central wavelength of the ENZ mode (~ 1460 nm), derived from the wave equation in the ITO layer, as explained in the Supporting Information, is demonstrated with solid lines. For the hybridized modes, the polariton branches are observable in Figure 2 as transmittance dips. While the upper polariton is clearly visible, the lower polariton dip in transmission is more subtle.

The white circles in Figures 2a and b represent the analytically obtained resonance positions, as explained in section 1 of the Supporting Information. We use Δf as a fitting parameter in our analytical model to minimize the deviation of the upper and lower polariton branches between the numerical simulation and analytical results. This value of Δf is equal to the spectral separation of hybrid modes at the dimension at which they are nearest to each other. We find that $\Delta f = 21$ THz for the EDR case and $\Delta f = 26$ THz for the MDR case. Comparing the magnitude of this anticrossing with the line widths of the resonances in the absence of ITO (around 12 THz) shows that the degree of anticrossing is significantly larger than the line widths of either Mie resonance in the absence of ITO, suggesting a strong coupling between those resonances and the ENZ mode. We note that this simple strong coupling theory describes the coupling of each Mie mode to the ENZ mode in a geometrically complex system. According to eq 1 of the Supporting Information, the ENZ mode's central frequency depends on the superstrate's

permittivity. In our case, the effective permittivity of the metasurface superstrate undergoes significant modification due to the antennas and their resonant conditions. Covering over 40% of the surface area and possessing substantial refractive indices, combined with non-negligible thicknesses, these antennas substantially alter the central frequency of the ENZ mode. That can explain the slight deviations in the analytical results from the simulation.

The details of the fabrication process are explained in section 2 of the Supporting Information. Figure 3a shows an SEM image of one of the fabricated devices. The samples were characterized in a wide-band linear measurement setup where a polarized uncollimated white light was focused on the samples and then recollimated to measure the transmittance of the metasurfaces on ITO. Figures 3b and c show the simulated and experimental transmittances of representative EDR and MDR samples, respectively. We observe a very good agreement between the experimental and simulation data in the magnitude of the anticrossings and the depth of the upper polariton branch, although there are some minor deviations in the resonance wavelengths and the transmittance. The deviations mostly arise from the uncertainty in the thickness of ITO at different locations of the samples. During fabrication, the dry etching process may have partially removed ITO from the exposed spaces between nanoantennas. Fabrication variations in the dimensions of the antennas could be another reason for deviations.

Figures 4a and b show the simulation and experimental results of the resonant wavelengths of different resonances as a function of dimensions. We extracted the position of the polariton branches in the experiment from the transmittance for each sample, as indicated by points in Figure 4a for the EDR case and Figure 4b for the MDR case. We observe a good agreement between the simulation and experiment for the EDR and MDR cases.

We have shown with simulations, analytical modeling, and experimental characterization that the two fundamental Mie modes of an a-Si metasurface, EDR and MDR, can strongly couple to the ENZ mode of a 23 nm layer of ITO. The main evidence for the strong coupling between the modes above is the avoided crossing of the hybrid modes of the metasurface over ITO that is larger than the line widths of the Mie modes

in the absence of ITO. The strength of the coupling and the depth of the resonances related to the hybrid modes could be further strengthened by using slightly thicker ITO layers to reduce the modal volume mismatch between the ENZ mode and the Mie modes.

Plasmonic metasurfaces that are strongly coupled to an ENZ mode of a TCO substrate have been shown to strongly enhance the nonlinear optical response of the ENZ material and thus create the opportunity for engineering dynamic, highly nonlinear metasurfaces.^{33,37,38} As a proof of principle for using the strongly coupled Mie–ENZ hybridized modes shown here in nonlinear applications, we performed degenerate pump–probe experiments, sketched schematically in Figure 5a, using 120 fs pulses. The pump pulses trigger a

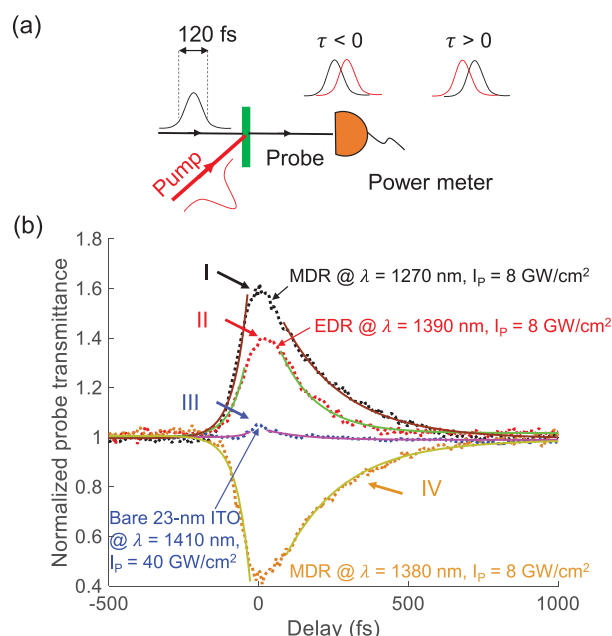


Figure 5. Nonlinear behavior of the samples. (a) A simple schematic of the time-resolving degenerate nonlinear measurement setup. An intense femtosecond (fs) pump beam triggers the nonlinear response of the sample, while a probe beam of the same duration interacts with the modified medium. (b) Normalized transmittance of the probe. The dotted lines show the normalized transmittance of a probe beam of light plotted with respect to the time delay between the pump and the probe for a bare 23 nm-thick ITO sample (in blue, curve III), one of the arrays in the EDR sample (in red, curve II), and one of the arrays in MDR sample at different incident wavelengths (1270 nm in black, curve I, and 1380 nm in brown, curve IV). Negative time delays mean that the probe precedes the pump at the sample. The solid curves represent the fitting results of the rising and falling edges of each curve to exponential equations to derive the rise and fall times of the induced nonlinear change in transmission. Curves I–IV exhibit rise times of 35, 49, 47, and –46 fs, and the slower relaxation times are 132, 130, 205, and 200 fs, respectively.

nonlinear response of the coupled sample of nanoantennas and ITO substrate similar to the plasmonic nanoantennas over ITO, which is then characterized by the transmittance of the weaker probe pulse at different relative timings to the pump.^{33,37} Note that the role of antennas is crucial here both because they confine more light into the ITO layer, as can be seen in Figure 1, and also because they allow for the light to couple from free space to the ENZ mode of the ITO layer.²⁴ In the presence of a strong pump, the coupling coefficients

between the Mie and ENZ modes are significantly perturbed due to the strong nonlinear optical response of the ITO substrate. As a consequence of the unity-order change in the refractive index of ITO, the spectral position and the strength of the hybrid modes also change as a function of the pump intensity, further enhancing the overall nonlinear response of the coupled system. Under such circumstances, the transmittance of a probe beam that travels through the sample may increase or decrease depending on the sign of frequency detuning, with respect to the resonant frequencies of the strongly coupled hybrid modes. The experimental results of the pump–probe measurements obtained from our samples are shown in Figure 5b. We recorded the change in transmittance of the frequency-degenerate probe as a function of the pump–probe delay and the pump–probe wavelengths. Figure 5b also shows results obtained in the same pump–probe setup for a bare 23 nm ITO sample. All of the metasurfaces show stronger modification (up to 20 times) in the transmitted power of the probe compared to what can be achieved for the bare 23 nm ITO sample, despite the metasurfaces being pumped with one-fifth the intensity used to pump the bare ITO sample. Thus, we measured a roughly 100-fold enhancement of the probe transmittance modulation in the metasurface. Such strong enhancement reinforces the notion that the metasurfaces achieve a stronger nonlinear response by enabling efficient coupling to the ENZ mode, enhancing the fields therein, and by time-varying changes in the resonant responses of the antennas due to nonlinear changes in ITO. We derived the rise and fall times of the induced nonlinear changes in transmission responses by fitting exponential equations to the experimentally obtained points (solid lines in Figure 5). We found that the rise time can be as short as 35 fs and the fall time can be as long as 205 fs.

The pump–probe responses of the MDR sample specifically show much richer dynamics than those observed for the EDR one. We measured both positive and negative changes in the probe transmittance, depending on the sign of the spectral detuning of the laser frequency from the MDR resonance. This richer response can be attributed to the stronger coupling of the MDR to the ENZ mode. A transmittance modulation of the same order of magnitude as in our case was reported using plasmonic metasurfaces over ITO.³³ However, the multi-resonant and collective natures of dielectric antennas allow the possibility of designing versatile, dynamic all-optical systems by engineering the interactions of each type of Mie mode with ENZ mode separately.³⁹ A comprehensive investigation of the nonlinear responses of these samples is beyond the scope of this work and is the subject of future research. We note that the speed of modification of the transmittance in our strongly coupled system of a-Si and ITO is at least one order of magnitude higher than the previously reported modification speeds of systems based on bare silicon.^{40,41} In addition, the nonlinear response of the Si–ENZ-based metasurfaces can be further enhanced by using ITO layers of critical thickness.⁴² The nonlinear response of an array of dielectric metasurface on a 33 nm ITO, where the EDR and the MDR both spectrally overlap at the ENZ region of the ITO layer, has been recently reported.⁴³ However, their discussion lacks the details of the role of each type of resonance in the modifications of the linear and nonlinear responses separately. The complete understanding of nonlinear dynamics of individual coupled Mie–ENZ resonances is essential for designing systems that exhibit richer spatiotemporal responses, for example, a time-varying

gradient metasurface that exploits the interactions of a group of Mie modes with a thin ENZ substrate.

In conclusion, we designed, simulated, fabricated, and tested a system to demonstrate strong coupling between the fundamental EDR and MDR Mie modes in an a-Si metasurface to the ENZ mode of a thin layer of ITO. Clear agreement among analytical, simulation, and experimental results confirmed that strong coupling of individual Mie resonances to the ENZ mode could be achieved, eliminating the concern that Mie resonances would have insufficient mode overlap with the ENZ mode to do so. Furthermore, we performed pump–probe nonlinear measurements that showed at least a 100-fold enhancement of transmission modulation through the metasurface in comparison to the already highly nonlinear bare ITO. The metasurface also seems to alter the subpicosecond onset and relaxation times of this modulation, although this relationship merits further investigation. Such coupled metasurface systems could be used for many applications requiring highly nonlinear responses with subpicosecond temporal modulation. While this was already known for plasmonic metasurfaces,^{33,37,38} the option for doing so with dielectric nanoantennas significantly expands the fabrication options. Potentially, even more importantly, it enables dynamically modulated coupling to higher-quality factor resonances and magnetic dipole modes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.3c03301>.

The initial section provides an in-depth exploration of the analytical formulation of the ENZ mode and the spectral placement of hybrid modes within a coupled system; the second section delves into the intricacies of device fabrication (PDF)

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Notes

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Supplementary Information

Interactions of fundamental Mie modes with thin epsilon-near-zero substrates

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Abstract

This document contains the supplemental information for the letter entitled "Interactions of fundamental Mie modes with thin epsilon-near-zero substrates". Section S1 presents the theoretical model used for fitting the data to the simulation results and extracting the frequency detunings due to the strong coupling effect. Section S2 provides information about the fabrication of the samples.

S1. Analytical Modeling

In our analytical model, the central wavelength of the ENZ mode was derived by solving the following dispersion relation of the modes in a thin layer of material with a permittivity of ε_1 sandwiched between two layers of permittivities ε_0 and ε_2 ¹ :

$$1 + \frac{\varepsilon_0 k_{z2}}{\varepsilon_2 k_{z0}} = i \tan(k_{z1} d) \left(\frac{\varepsilon_1 k_{z2}}{\varepsilon_2 k_{z1}} + \frac{\varepsilon_0 k_{z1}}{\varepsilon_1 k_{z0}} \right) \quad (1)$$

where $k_{zi}^2 = \varepsilon_i \frac{\omega^2}{c^2} - k_{\parallel}^2$, $k_{\parallel}$ is the transverse wavenumber; ω is the angular frequency; d is the thickness of the middle layer; and c is the speed of light in vacuum. To solve these equations, we used the permittivity of ITO derived from the ellipsometry data. We found that the central wavelength of the ENZ mode is around 1460 nm. Note that this wavelength is different from the point where the real part of permittivity vanishes, although they are near each other.

To analyze the strongly coupled system, we used the theory explained in previous works.^{2,3} According to this model, the frequencies of the lower and upper branches after the coupling can be calculated as a function of the isolated resonance frequencies using the following relations:

$$\omega_{\pm} = \frac{1}{2}(\omega_{\text{DR}} + \omega_{\text{ENZ}} \pm \sqrt{(\omega_{\text{DR}} - \omega_{\text{ENZ}})^2 + 4\Delta^2}) \quad (2)$$

where $\Delta = 2\pi\Delta f$ is the angular frequency difference between the split modes; ω_+ and ω_- are the frequencies of the hybrid modes of upper and lower polariton branches, respectively; and ω_{DR} and ω_{ENZ} are the resonance frequencies for the dipole resonances and the ENZ mode, respectively. The white circles in Figures 2(a) and 2(b) in the main text represent the analytically obtained resonances. We use Δf as a fitting parameter in our analytical model to minimize the deviation of the upper and lower polariton branches between the numerical simulation and the analytical results. This value of Δf is equal to the spectral separation of hybrid modes at the dimension that they are nearest to each other.

S2. Fabrication Process

We fabricated structures with different antennas/lattice dimensions to study the coupling of the EDR/MDR to the ENZ mode. A 23 nm-thick ITO on SiO₂ samples was obtained from a commercial source. The ITO samples were cleaned, followed by deposition of 230 nm a-Si via PECVD at 1000 mT, 210 oC with an RF power of 10 W using 25 sccm Silane and 475 sccm of Argon. To pattern the metasurface into the a-Si layer, a spin-coat of 500 nm Zep-520a (a positive-tone EBL resist) was hard baked at 180 oC for 2 min, then was exposed using a 100 keV EBL system with a dosage of 210 $\mu\text{C}/\text{cm}^2$ followed by development in N-Amy Acetate for 1 min. The pattern is then transfered into the a-Si layer by ICP-RIE a pressure of 10 mT, temperature of 20 oC, ICP power of 100 W, and RIE power of 20 W with 30 sccm of C₄F₈ and 20 sccm of SF₆. Residual Zep resist was then removed using acetone before inspection of the samples using optical and electron microscopes. Figure 3(a) in the main text shows the SEM image of one of the fabricated devices.

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