Space-time duality in paraxial optical wave propagation implies the existence of intriguing effects when light interacts with a material exhibiting two refractive indexes separated by a boundary in time. The direct consequence of such time-refraction effect is a change in the frequency of light while leaving the wavevector unchanged. Here, we experimentally show that the effect of time refraction is significantly enhanced in an epsilon-near-zero (ENZ) medium as a consequence of the optically induced unity-order refractive index change in a sub-picosecond time scale. Specifically, we demonstrate broadband and controllable shift (up to 14.9 THz) in the frequency of a light beam using a time-varying subwavelength-thick indium tin oxide (ITO) film in its ENZ spectral range. Our findings hint at the possibility of designing (3 + 1)D metamaterials by incorporating time-varying bulk ENZ materials, and they present a unique playground to investigate various novel effects in the time domain.
Maxwell’s equations describe how an electromagnetic wave is modified by a material. The spatial boundary condition associated with Maxwell’s equations can be used to derive the well-known Fresnel equations and Snell’s law. A spatial variation in refractive index leads to reflection and refraction of a light beam incident on the boundary. As a consequence, the wavevector of the transmitted light changes, whereas the frequency is conserved. The spatial boundary can be abrupt (nonadiabatic) in refractive index variation such as at a spatial boundary (left panel). Here $f$ is the frequency of light waves in the medium. The permittivity of an ITO film used in the experiment. The inset shows the simplified experimental setup and the shaded region shows the spectral range of interest in this work. The frequency of the probe redshifts (blueshifts) if the pump beam lags (leads) the probe. At near-zero delay both redshift and blueshift can occur.

Results

Nonlinear optical response of the ENZ material. An ENZ material is defined as a medium that has a near-zero linear permittivity, and consequently low linear refractive index. The near-zero permittivity in such a medium leads to highly nonlinear optical interactions. To overcome these shortcomings by using a homogeneous and isotropic epsilon-near-zero (ENZ) medium of subwavelength thickness. Using a series of pump-probe measurements, we demonstrate optically controlled total frequency translations of a near-infrared beam of up to 14.9 THz (redshift of 11.1 THz and blueshift of 3.8 THz)—that is, over 6% of the bandwidth of the carrier frequency—using a 620-nm-thick ITO film. The effect of frequency translation is broadband in nature, i.e., the central wavelength of the degenerate input pump and probe pulses can be tuned over a 500 nm range. We also find that the effect is maximum near the zero-permittivity wavelength of ITO.

The inset shows the simplified experimental setup and the shaded region shows the spectral range of interest in this work. The frequency of the probe redshifts (blueshifts) if the pump beam lags (leads) the probe. At near-zero delay both redshift and blueshift can occur.
With a large index change, we make use of the large and ultrafast optically induced change in refractive index of a 620 nm thick ITO film in its near-zero-permittivity spectral range. ITO is a degenerately doped semiconductor and near its zero-permittivity wavelength (1240 nm), the linear permittivity of the ITO sample can be well described by the Drude model (Fig. 1b). The temporal nonlinear optical response of ITO can be described by the two-temperature model when excited by an optical pulse with a central wavelength (1240 nm), the linear permittivity of the ITO sample is limited by the thermalization time of the conduction band electrons owing to electron-electron scattering. The rise time also depends on the energy deposition rate in the ITO band electrons owing to the momentum-dependent effective mass of the electrons. According to the two-temperature model, the rise time of the change in the refractive index is limited by the thermalization time of the conduction band electrons owing to electron-electron scattering. The rise time also depends on the energy deposition rate in the ITO film and thus has a strong dependence on the temporal envelope of the pump pulse. Once the pump pulse peak leaves the ITO film, the index returns to the initial value within a sub-picosecond time scale through electron–phonon coupling (Fig. 1c). Owing to the time-dependent nature of the index change induced by the intensity of the pump pulse, the frequency of probe pulse can be redshifted or blueshifted depending on the pump-probe delay time (see Fig. 1d).

Measurements at the near-zero-permittivity wavelength. In order to measure the magnitude of the frequency translation using ITO, we performed a set of degenerate pump-probe experiments with ~120 fs pulses and recorded the spectra of the probe beam as a function of the delay between the pump and the probe for varying pump intensities. The ITO film has two 1.1-mm-thick glass slabs on both sides. Both pump and probe beams are p-polarized, and the intensity of the probe beam is kept low to avoid nonlinear effects (See Methods and Supplementary Note 1 for more details). The results for \( \lambda_0 = \lambda_{\text{pump}} = \lambda_{\text{probe}} = 1235 \) nm at the pump-probe delay time of ±60 fs is shown in Fig. 2. The pump induces a nonlinear change in the refractive index of ITO with a rate that depends on the pump intensity, the temporal envelope of the pump, and the intrinsic nonlinear dynamics of the ITO. When the pump pulse is delayed with respect to the probe, i.e., pump-probe delay time \( t_d < 0 \), the probe experiences a rising refractive index and thus its spectrum redshifts (Fig. 2a). If the probe reaches the ITO after the peak of the pump pulse is passed \( (t_d > 0) \), it experiences a falling refractive index change and the spectrum of the probe blueshifts (Fig. 2b). We also note that for \( t_d = 0 \) both blueshift and redshift can occur (Fig. 1d). As the thickness of the ITO film is only 620 nm, 120 fs pump, and the probe pulses never reside entirely within the ITO thin film (Fig. 1d). Thus, the magnitude of the frequency shift of the probe pulse becomes dependent on the index change rate \( \Delta n/\Delta t \) it experiences while transiting through the ITO film. We extract the effective values of the index change rate based on the experimental data through numerical simulations (see Supplementary Note 2). In numerical simulation we use the slowly varying envelope approximation and, as a result, the predictions of our model are only dependent on the envelope-averaged dynamics of the ITO.

We find that both the pump intensity and the value of the pump-probe delay time modify the spectra of the transmitted probe. We present the results for \( \lambda_0 = 1235 \) nm for three pump intensities in Fig. 3a–c. In general, the time refraction leads to the modification of amplitude, bandwidth, temporal width, and the carrier frequency of the probe pulse (see Supplementary Note 3). In order to focus on the spectral shift, the magnitude of spectrum for each pump-probe delay value is individually normalized in Fig. 3. We find that when the absolute value of the pump-probe delay time \( |t_d| \) is increased, the magnitude of the frequency translation for the probe decreases. Furthermore, when pump-probe delays are small, the leading portion of the probe pulse experiences an increase in refractive index (thus redshifts), whereas the trailing portion experiences a decrease of refractive index (thus blueshifts). This is evident in Fig. 3a–c by the presence of two peaks at \( t_d = 0 \). For a fixed pump-probe delay time an increase in pump intensity leads to larger change in index and, as a result, a larger shift in the central frequency of the probe pulse. Furthermore, we find that the fall time of the index change is slower than the rise time of the index change. The fall time of the index change is longer because it—within the formalism of the two-temperature model—is dictated by the intrinsic electron–phonon coupling rate, the maximum temperature of the conduction band electrons, and the thermodynamical properties of the lattice. As a result, the rate of decrease in index after the pump leaves the ITO film is smaller compared with that of the rising edge, and therefore the magnitude of the achievable redshift for a constant pump intensity is larger than the achievable blueshift. At a sufficiently high pump intensity, we observe an appearance of a large blueshifted spectral peak when the pump is at 1235 nm owing to higher-order nonlinear optical effects. At a peak pump intensity of 483 GW cm\(^{-2}\) the blueshift can be as large as 10.6 THz (~52 nm in wavelength), and the total maximum frequency translation can be larger than 20 THz (see Supplementary Note 4). This value corresponds to a fractional frequency shift \( (\Delta f_0/ f_0) \) of ~9%.

We model the time-refraction effect in ITO using the nonlinear Schrödinger equation, and the split-step Fourier method is used to numerically solve the Schrödinger equation. We use an iterative algorithm to calculate the approximate shape of the time-varying nonlinear phase variations induced by the index change to fit the experimentally measured spectra (see Supplementary Note 2). The simulation results are shown in Fig. 3d–f. Our numerical model is in excellent agreement with the experimental data, confirming that the origin of the shift is owing to the rapid change of index experienced by the probe pulse while transiting through the ITO sample.
Measurements over a broad spectral range. Next, we investigate the dynamics away from the zero-permittivity wavelengths. We repeat the measurements at different excitation wavelengths from $\lambda_0 = 1000\,\text{nm}$–$1500\,\text{nm}$. For each excitation wavelength and pump intensity, we extract the maximum frequency translation of the probe over a range of pump-probe delay time (see Supplementary Note 5). We summarize the wavelength- and intensity-dependent maximum frequency translations in Fig. 4a–e. Here, we limit the pump intensities to avoid the occurrence of significant higher-order nonlinearities. Our results reveal a number of trends. First, both the total achievable frequency translation (redshift and blueshift) and the maximum achievable redshift for a constant pump intensity are the highest near 1235 nm (redshift plus blueshift) is $10.8\,\text{THz}$.

Fig. 3 Experimental and simulated probe spectra at $\lambda_0 = 1235\,\text{nm}$. a–c Experimental probe spectra as a function of the pump-probe delay time for varying pump intensities. The spectral magnitude for each pump-probe delay is normalized individually. d–f The corresponding numerically simulated probe spectra modeled by the nonlinear Schrödinger equation. The spectra of the probe show a strong dependence on the pump intensity and pump-probe delay time. For a pump intensity of $268\,\text{GW/cm}^2$, the total frequency translation at this wavelength is $10.8\,\text{THz}$.

Discussion

As the refractive index of the ENZ material depends on the intensity of the pump, the work presented here may be formally described by cross-phase modulation with a delayed response. However, the concept of time refraction is independent of the source type of the index change (e.g., thermally, optomechanically, or electrically induced index change) and is a more general effect than the simple cross-phase modulation that arises when the temporal boundary is specified, or electrically induced index change) and is a more general effect than the simple cross-phase modulation that arises when the temporal boundary is specified, or electrically induced index change. Moreover, in contrast to a typical four-wave-mixing-based frequency conversion, the frequency shift obtained through time refraction does not depend on the frequency difference between the pump and the probe and is completely free from phase-mismatching. Although in this work the pump and the probe are frequency degenerate and produced from the same source using a beam splitter, it is not necessary for the beams to be frequency degenerate. Nevertheless, the maximum frequency shift with minimum energy expenditure can be achieved when both the pump and the probe lie within the ENZ spectral range. As the maximum index change happens at the zero-permittivity wavelength, the probe will undergo maximum frequency shift if its wavelength is at or near the zero-permittivity wavelength, whereas the energy expenditure will be...
Fig. 4 Wavelength-dependent time-refraction effect. a–e Experimentally measured maximum redshifts and blueshifts at different wavelengths $\lambda_0$ as a function of peak pump intensities. f The red line denotes the fractional redshift $|\Delta f_{\text{red}}|/f_0$ as a function of probe beam’s central frequency $f_0$ at a peak pump intensity $450 \text{ GW cm}^{-2}$. The real part of the linear permittivity $\Re(\epsilon)$ of ITO film at the corresponding central frequency $f_0$ is shown in the top axis. The black line shows the total fractional shift (redshift plus blueshift) measured at the maximum pump intensities before the onset of higher-order nonlinear optical effects. We find that both the maximum fractional redshift and the total shift occur near the zero-permittivity wavelength.

minimum if the wavelength of pump is also at or near the zero-permittivity wavelength.

In conclusion, we have shown that a subwavelength-thick ITO film can be used to obtain unprecedentedly large (~6.5% of the carrier frequency), broadband and tunable frequency translation. The large time-refraction effect in the ENZ material raises the intriguing possibility of wavelength conversion over an octave using a time-varying ENZ medium. The magnitude of the frequency translation is primarily limited by the linear loss, higher-order nonlinear optical effects, dispersion, and the interplay between the pulse width and the interaction time. We note that the ENZ spectral region of ITO and other conducting oxides can be tuned at any wavelength between 1 µm and 3 µm by choosing the appropriate doping level. Furthermore, because the effect is present in a bulk, homogeneous and isotropic material, one can engineer nanostructures incorporating ENZ media such as plasmonic waveguides, photonic crystal waveguides, and dynamic metasurfaces to arbitrarily control the sign and the magnitude of the frequency shift in order to build efficient octave-spanning frequency tuners while simultaneously lowering the required pump power by a few orders of magnitude. For example, an appropriately engineered ITO-based platform can be used to shift an entire band of optical signals in the frequency domain. Such devices may find practical usage in quantum communication protocols requiring conversion of visible photons to infrared and in classical coherent optical communications. We anticipate that the large time-refraction effect, we report here, can be exploited to engineer magnet-free nonreciprocal devices and spatiotemporal metasurfaces, and to investigate photonic time crystals and other topological effects in the time domain using free-space or on-chip ENZ-based structures.

**Methods**

**Measurements.** We use a tunable optical parametric amplifier (OPA) pumped by an amplified Ti:sapphire laser of ~120 fs for the experiments. The output of the OPA is split into two beams to produce the degenerate pump and probe beams using a pellicle beam splitter. Both beams are rendered $p$-polarized. The pump beam is focused onto the sample by a 25 cm lens yielding to a spot size of ~100 µm. The probe beam is focused by a 10 cm lens and its spot diameter is ~45 µm at 1235 nm. Although the spot size can change when the wavelength of the OPA output is adjusted, we always keep the probe beam spot size significantly smaller than the pump beam so that the probe beam experiences a nearly uniform change in the refractive index in the transverse dimensions. The angles of incidences are 15° and 10° for the pump and probe, respectively. The transmitted probe light is coupled to an optical spectrum analyzer via a multimode fiber with a 50 µm core diameter. The commercially available ITO thin film (PGO GmbH) has a thickness of 310 nm and is deposited on a 1.1-mm-thick glass substrate. We sandwich two such ITO films to make the 620 nm thick ITO sample by using a customized sample holder with adjustable tightening screws (See Supplementary Note 6). We use a translation stage to control the delay time between the pump and the probe beams. The experimental setup is presented in Supplementary Note 1.

**Data availability**

All data supporting this study are available from the corresponding author upon request.

**Code availability**

All relevant computer codes supporting this study are available from the corresponding author upon request.

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**References**

1. Akhmanov, S., Sukhorukov, A. & Chirkin, A. Nonstationary phenomena and space-time analogy in nonlinear optics. Sov. Phys. JETP **28**, 748–757 (1969).
2. Kolner, B. H. Space-time duality and the theory of temporal imaging. IEEE J. Quant. Electron. **30**, 1951–1963 (1994).
3. Xiao, Y., Maywar, D. N. & Agrawal, G. P. Reflection and transmission of electromagnetic waves at a temporal boundary. Opt. Lett. **39**, 574–577 (2014).
4. Xiao, Y., Agrawal, G. P. & Maywar, D. N. Spectral and temporal changes of optical pulses propagating through time-varying linear media. Opt. Lett. **36**, 505–507 (2011).
5. Plansinis, B. W., Donaldson, W. R. & Agrawal, G. P. What is the temporal analog of reflection and refraction of optical beams? Phys. Rev. Lett. 115, 183901 (2015).

6. Mendonca, J., Guerreiro, A. & Martins, A. M. Quantum theory of time refraction. Phys. Rev. A 62, 033805 (2000).

7. Mendonca, J. & Guerreiro, A. Time refraction and the quantum properties of vacuum. Phys. Rev. A 72, 063805 (2005).

8. Boyd, R. W. Nonlinear optics. 3rd edn (Elsevier, 2003).

9. Alam, M. Z., Schulz, S. A., Upham, J., De Leon, I. & Boyd, R. W. Large optical nonlinearity of nanoantennas coupled to an epsilon-near-zero material. Nat. Photonics 12, 79–83 (2018).

10. Caspani, L. et al. Enhanced nonlinear refractive index in -near-zero materials. Phys. Rev. Lett. 116, 233901 (2016).

11. Rezai, O., De Leon, I., Alam, M. Z. & Boyd, R. W. Nonlinear optical effects in epsilon-near-zero media. Nat. Rev. Mat. 4, 535–551 (2019).

12. Yu, Z. & Fan, S. Complete optical isolation created by indirect interband photonic transitions. Nat. Photonics 3, 91–94 (2009).

13. Shaltout, A. M., Shalaev, V. M. & Brongersma, M. L. Spatiotemporal light control with active metasurfaces. Science 364, eaat3100 (2019).

14. W. R. Boyd, J. M. Pendry, J. Topological aspects of photonic time reversal. Nat. Photonics 3, 293–296 (2009).

15. Yacomotti, A. M. et al. Nonadiabatic dynamics of the electromagnetic field on a femtosecond time scale. Phys. Rev. A 88, 011802 (2013).

16. Lustig, E., Sharabi, Y. & Segev, M. Topological aspects of photonic time reversal. Nat. Photonics 3, 293–296 (2009).

17. Caspani, L. et al. Enhanced nonlinear refractive index in -near-zero materials. Phys. Rev. Lett. 116, 233901 (2016).

18. Agrawal, G. P. Nonlinear fiber optics. In Nonlinear Science at the Dawn of the 21st Century. Lecture Notes in Physics, Vol. 542 (Springer, 2000).

19. Guo, Y. et al. Towards integrated metanetworks: a holistic approach on precise optical and electrical properties of indium tin oxide. Sci. Rep. 9, 1–10 (2019).

20. Kimsey, N. et al. Epsilon-near-zero-al-doped zno for ultrafast switching at telecom wavelengths. Optica 2, 616–622 (2015).

21. Li, Q., Davanço, M. & Srinivasan, K. Efficient and low-noise single-photon frequency shifter. Nat. Photonics 10, 766–770 (2016).

22. DeHaye, P. et al. Optical frequency comb generation from a monolithic microring resonator. Nature 450, 1214–1217 (2007).

23. Lopes, N. et al. Laser pulse frequency up-shifts by relativistic ionization fronts. Europhys. Lett. 66, 371–377 (2004).

24. Fan, L. et al. Integrated optomechanical single-photon frequency shifter. Nat. Photonics 10, 406–416 (2016).

25. Gaafar, M. A. et al. Reflection from a free carrier front via an intraband indirect photonic transition. Nat. Commun. 9, 1447 (2018).

26. Beggs, D. M., Krauss, T. F., Kuipers, L. & Kampfrath, T. Ultrafast tilting of the dispersion of a photonic crystal and adiabatic spectral compression of light pulses. Phys. Rev. Lett. 108, 033902 (2012).

27. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

28. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

29. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

30. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

31. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

32. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

33. Fan, L. et al. Integrated optomechanical single-photon frequency shifter. Nat. Photonics 10, 406–416 (2016).

34. Gaafar, M. A. et al. Reflection from a free carrier front via an intraband indirect photonic transition. Nat. Commun. 9, 1447 (2018).

35. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

36. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

37. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

38. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

39. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

40. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

41. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

42. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

43. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

44. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

45. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

46. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

47. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

48. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

49. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

50. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

51. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

52. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

53. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

54. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).

55. Cabo, R. et al. Tunable all-optical switching using a semiconducting photonic crystal. Appl. Phys. Lett. 105, 151107 (2014).

56. Lee, K. et al. Linear frequency conversion via sudden merging of meta-atoms in time-variable metasurfaces. Nat. Photonics 12, 765–773 (2018).

57. Scherbakov, M. R. et al. Photon acceleration and tunable broadband harmonics generation in nonlinear time-dependent metasurfaces. Nat. Commun. 10, 1345 (2019).
