Organic metallic epsilon-near-zero materials with large ultrafast optical nonlinearity

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Epsilon-near-zero (ENZ) materials have shown significant potential for nonlinear optical applications due to their ultrafast hot carriers and consequent optical nonlinearity enhancement. Modified poly(3,4-ethylenedioxythiophene) (PEDOT) films show metallic characteristics and a resultant ENZ wavelength near 1550nm through polar solvent treatment and annealing. The metallic PEDOT film exhibits an intrinsic optical nonlinear response that is comparable to gold and 100-fold higher than typical inorganic semiconductor ENZ materials due to π-conjugated delocalized electrons. The excitation of hot carriers further enhances its optical nonlinearity factor by a factor of 22 at 1550 nm. Hot holes in metallic PEDOT films have a smaller enhancement multiple of carrier temperature and a longer relaxation time than hot electrons in inorganic ENZ materials due to the larger imaginary permittivity and hot-phonon bottleneck for carrier cooling. Our findings suggest that π-conjugated ENZ polymer may have unique ultrafast and nonlinear optical properties compared to inorganic ENZ materials, enabling new possibilities in on-chip nanophotonic devices, nonlinear optics, and plasmonics.

Keywords: Epsilon-near-zero; organic optical nonlinearity; hot carrier

INTRODUCTION

Epsilon-near-zero (ENZ) materials have recently attracted considerable attention because of their enhanced ultrafast optical nonlinearity in the ENZ wavelength range[1–3] and been used in applications such as time-varying medium[4–7], harmonic generation[8, 9] and ultrafast switching[10–12]. Among ENZ materials, semiconductor materials, especially transparent conductive oxides (TCOs), can achieve ENZ wavelengths located in the optical communication band and up to thousands of times increased optical nonlinear response due to their low optical loss and substantially tunable carrier concentration[1]. Their intrinsic nonlinearity, however, is somewhat modest, thus posing stringent requirements for the operating conditions of nonlinear devices based on semiconductor ENZ materials. In contrast, noble metal ENZ materials, such as gold and silver, have extremely high carrier concentrations and ENZ wavelengths in the visible band, and can produce high intrinsic optical nonlinear responses because of the delocalized electrons distributed inside the material. Nevertheless, the high optical loss of metals at the ENZ wavelength and the difficulty of tuning optical properties precludes us from further enhancing the nonlinear response of the metal. Consequently, we anticipate discovering a material with high intrinsic optical nonlinearity, low optical loss, and obvious ENZ-induced nonlinearity enhancement behavior, which may lead to “super optical nonlinearity”.

The great intrinsic nonlinearity of metals originates from the fact that the delocalized electrons are less tightly bound and thus respond more freely to the applied optical field[13]. In addition to being found in noble metals, such delocalized electrons are also widely present in a particularly significant type of organic compounds: π-conjugated polymers. Therefore, π-conjugated polymers have the potential to exhibit a significant level of intrinsic optical nonlinearity. Furthermore, a straightforward calculation of the Drude model \( \omega_p = \sqrt{(ne^2)/(\varepsilon_0 m^* \pi)} \) reveals that the higher the carrier concentration, the higher the plasma frequency, and hence the greater likelihood that the ENZ wavelength will be in the near infrared. As is commonly known, ENZ materials that can be employed in the optical communication band are crucial for the integrated nonlinear optical devices.

Therefore, poly(3,4-ethylenedioxythiophene) (PEDOT), a π-conjugated polymer that has been extensively utilized in studies and can attain a maximum carrier concentration of \( 10^{21} \text{cm}^{-3} \) (\( 10^{22} \text{cm}^{-3} \) for metals), is researched detailed by us. Here, by ethylene glycol pre-treatment as well as annealing, metallic PEDOT films can achieve 250-fold greater electrical conductivity than pristine PEDOT, Fermi level into the valence band, improved crystallites and a resultant ENZ wavelength near 1550nm. Z-scan experiments show that the metallic PEDOT films indeed possess an intrinsic nonlinearity comparable to that of gold and 100 times higher than that of the typical inorganic semiconductor ENZ material, indium tin oxide (ITO). Hot-carrier-induced ENZ nonlinearity enhancement is multiplied up to 22 times in metallic PEDOT films. The hot holes dynamics of PEDOT demonstrate that the hot carrier relaxation period in PEDOT is longer than in inorganic ENZ materials due to the hot-phonon bottleneck of PEDOT.
RESULTS

Preparation and characterization of PEDOT film

In PEDOT, the \(\pi\)-bond formed by overlapping p orbitals of multiple atoms enables the delocalization of electrons within the conjugate bond, indicating that PEDOT is capable of achieving substantial intrinsic optical nonlinearities\(^\text{[13]}\). In addition, to realize ENZ wavelengths located in the NIR, we employed ethylene glycol (EG) to separate PEDOT component from the PEDOT: PSS solution, and then dropped the extracted PEDOT solution to the glass substrate and dry annealed it under controlled conditions (Details in Methods). During the annealing process, water evaporation results in the concentration of PEDOT and allows recrystallization during the annealing process, water evaporation results in the annealing process, the thickness of the same sample varies widely between the center and edge regions, as shown in Fig. 1(c). Fig. 1(b) demonstrates the microscopic surface morphology of PEDOT. The formation of a PEDOT nanofibril-based network following dry annealing demonstrates well-ordered crystallites separated from each other by a less-ordered ‘amorphous’ matrix\(^\text{[15]}\). Finally, we get a PEDOT film with a preferred molecular alignment orientation and crystallinity that is superior to that of a pristine PEDOT: PSS film prepared by spinning (Fig. 1(e)). The XRD pattern shown in Fig. 1(e) for the pristine PEDOT: PSS film (blue line) displays two characteristic peaks at 17.7\(^\circ\)(\(d = 5.0\text{Å}\)) and 25.78\(^\circ\)(\(d_{010} = 3.5\text{Å}\)). They are indexed to the amorphous halo of PSS component, and the \(\pi\)-\(\pi\) stacking along (010) of the PEDOT thiophene ring, respectively. In the XRD pattern of modified PEDOT (orange line), two new unique distinctive peaks (2\(\theta = 6.96\)\(^\circ\) and 12.32\(^\circ\)) emerge as a result of the chain rearrangement of PEDOT with the decreased PSS component (Fig. 1(e)). The first and second reflections of the alternative inter-lamella stacking distance of the PEDOT molecule are allocated to these two peaks. The \(d_{100}\) and \(d_{200}\) peaks of modified PEDOT film represent that by diminishing PSS components, the inter-lamella charge hopping distance may be reduced, leading to increased electrical conductivity\(^\text{[16, 17]}\).

Meanwhile, the increasing intensity and sharpness of the \(d_{100}\) and \(d_{200}\) peaks indicate a structural change from amorphous to a ‘weakly ordered polymer aggregates’ in PEDOT. Consequently, the modified PEDOT films exhibit a carrier mobility of \(5.8cm^2\cdot V^{-1}\cdot s^{-1}\) and a carrier concentration \(n = 1.037 \times 10^{21}cm^{-3}\), 250 times and 10 times higher than the pristine PEDOT: PSS, respectively (Fig. 1(a) and Table. 1). According to the Drude model, increasing the carrier concentration \(n\) causes the plasmon frequency \(\omega_p\) to blueshift.

\[
\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0m^*}} \propto \sqrt{n}
\]

where \(e\), \(\varepsilon_0\), and \(m^*\) represent, electron charge, vacuum permittivity, and effective mass of free carriers, respectively. Thus, the modified PEDOT film with a 10 times higher carrier concentration \(n\) will have a 3.3 times larger plasmon frequency \(\omega_p\). Although we obtain the permittivity of PEDOT\(^\text{[18]}\) using the Drude-Lorentz model rather than the pure Drude model, the ENZ frequency \(\omega_{ENZ}\) remains roughly proportional to the square root of the carrier concentration \(n\). Thus, the measured permittivity (Table. 1) shows that the modified PEDOT film has an ENZ wavelength \(\lambda_{ENZ} = 1587nm\) (Fig. 1(f)), whereas the pristine PEDOT: PSS film has an ENZ wavelength \(\lambda_{ENZ} = 5267nm\) (Fig. 1(d)).

ENZ materials are well known for their ultrafast and huge optical nonlinearity. Before investigating the ultrafast features of PEDOT, its energy band structure must be understood. Therefore, ultraviolet photoelectron spectroscopy (UPS) and UV-visible absorption spec-
tra are utilized to determine the energy characteristics of the valence electrons within the material. Fig. 2(a) and 2(b) demonstrate the highest occupied molecular orbital (HOMO) and Fermi level positions of modified PEDOT relative to the vacuum energy level, respectively. The secondary electron cut-off (SECO) in Fig. 2(a) gives the work function \( q \phi_p = 5 eV \) for PEDOT, which is consistent with the HOMO energy range of most PEDOT: PSS films (5eV-5.2eV). Due to the high doping concentration exhibited by modified PEDOT (\( \sim 10^{21} \text{cm}^{-3} \)), its Fermi level is located at 90 meV below the top of the valence band [19, 20]. The direct bandgap is determined using the Tauc plot. The square of the product of the absorption coefficient and photon energy \( (\alpha h \nu)^2 \) is plotted against the photon energy \( h \nu \) in Fig. 2(c). Because of the Tauc relationship \( (\alpha h \nu)^2 = \beta (h \nu - E_g) \), the direct optical bandgap \( E_g \) equals the value of the transverse intercept determined by extrapolating the linear region. Fig. 2(d) depicts the semiconductor energy band structure of this modified PEDOT, which has a direct optical bandgap of 3.81eV. This value is close to the bandgap of EG-treated PEDOT: PSS reported by V. Singh [21]. In addition, the low thermoelectric characteristics (\( S = 12.6 \mu V/K \)) maintained by PEDOT:PSS with high conductivity indicate that it is closer to a material with polaron network (metallic) than to one with bipolaron network (semi-metallic) [22]. Hence, these features indicate the metallic nature of the modified PEDOT material.

**Ultrafast nonlinearity of metallic PEDOT film**

ENZ materials show an increased optical nonlinear response as the incidence angle increases within a certain range [1]. To explore the effect of ENZ on optical nonlinearity in organic ENZ materials, we used the Z-scan technique to assess ENZ nonlinear optical properties of metallic PEDOT films. As depicted in Fig. 3(a) and 3(b), both closed- and open-aperture measurements were performed within the ENZ region and incident angles of 0°, 20°, 30°, 40° to obtain the ENZ optical nonlinearity while the Z-scan signals were measured out of the ENZ region to obtain the intrinsic optical nonlinearity. As the angle increases, the spot size becomes larger and larger. Since the thickness of our samples is not uniformly distributed (Fig. 1(c)), a large spot can lead to excessive thickness variation within the spot area, which affects the stability of open- and closed-aperture optical signals. This is why we only provide the measurement value up to 40° in Fig. 3(c) and 3(d). It is worth noting that the normalized transmittance for closed-aperture measurements exhibits an asymmetric peak profile, which increases with incidence angle due to the increasing sample absorption [1].

We retrieved the nonlinear refractive index \( n_2 \) and nonlinear absorption coefficient \( \alpha_2 \) from closed- and open-aperture transmittance signals using formulas mentioned in the Supplementary Information. Fig. 3(c) and 3(f) show \( n_2 \) and \( \alpha_2 \) and their enhancement factor as a function of the angle of incidence \( \theta \) at 1550nm (inside the ENZ wavelength region). The enhancement factor is defined relative to the value outside the ENZ spectral region (at \( \lambda = 1300nm \)) at normal incidence, which is the ratio of ENZ to intrinsic optical nonlinear responses. The enhancement tends to rise with \( \theta \) for the entire measurement range (\( 0^\circ < \theta < 40^\circ \)). The maximum enhancement factors for PEDOT, measured at \( \theta = 40^\circ \), are 22.80 and 21.78 for \( n_2 \) and \( \alpha_2 \), and the corresponding values (\( n_2, PEDOT = 1.062 \times 10^{-14} \text{m}^2/\text{W} \) and \( \alpha_2, PEDOT =...
FIG. 3. Hot-holes-induced optical nonlinearity enhancement for metallic PEDOT films. (a) Real permittivity of metallic PEDOT: PSS. The blue wavelength is out of the ENZ region while the red wavelength is inside the ENZ region. (b) Different excitation method for intrinsic and ENZ optical nonlinearity. Normal incident light with non-ENZ wavelength (blue) is used to excite intrinsic optical nonlinear response while the oblique incident light with ENZ wavelength (red) is used to excite ENZ optical nonlinearity within ENZ region. The optical nonlinearity within ENZ region is boosted by hot holes in PEDOT. The ENZ optical nonlinear response. The optical nonlinearity within ENZ region is boosted by hot holes in PEDOT. (c) Closed- and open-aperture Z-scan signals at $\lambda = 1550\text{nm}$ and $\theta = 0^\circ, 20^\circ, 30^\circ, 40^\circ$ for the modified PEDOT film with an ENZ wavelength of 1587nm. The solid lines represent the theoretical fits to the experimental data. The value and enhancement factor of (e) nonlinear refractive index $n_2$ and (f) nonlinear absorption coefficient $\alpha_2$ at 1550nm. Enhancement factor is defined as the ratio of ENZ to intrinsic optical nonlinear responses (g) Diagram for the excitation and cooling of hot holes in PEDOT. (h) Simulated electron and lattice temperature evolution process in two-temperature model. (i) Measured normalized transient absorbance $\Delta A$ of PEDOT via pump-probe techniques. The three prediction results are from the two-temperature model and bi-exponential fitting, respectively. The pump-probe configuration: 100kHz repetition frequency, 370fs pulse duration, pump wavelength of 515nm (2.4eV) and probe wavelength of 1300 nm (0.95eV). The bi-exponential fitting model is $A_{\text{exp}}[1 - \exp(-t/\tau_{\text{OP}})] + B_{\text{exp}}[1 - \exp(-t/\tau_{\text{AP}})]$ and A over B is 9:1. The red, orange and green region corresponds to thermalization, emission of optical phonons $\tau_{\text{OP}}$, and optical-phonon interaction $\tau_{\text{OP-AP}}$.}

$-4.33 \times 10^{-8} m/W$ are approximately equal to ITO’s maximum values measured at ENZ wavelengths and oblique incidence $n_{2,\text{ITO}} = 1.1 \times 10^{-14} m^2/W$ and $\alpha_{2,\text{ITO}} = -7 \times 10^{-8} m/W$. The observed nonlinearity dependent on the angle of incidence is mostly due to a modification of the energy distribution of carriers as a consequence of the laser-induced carrier heating, also referred to as hot carriers. The mechanism of this kind of ENZ-induced optical nonlinearity enhancement has been well described using a two-temperature model. This model has been effectively employed to explain the ultrafast nonlinear response of metals and semiconductor ENZ materials irradiated by femtosecond pulses[1, 23–26].

To validate the two-temperature model for PEDOT, a non-degenerate pump-probe system is configured using a 515nm pulsed laser with the pulse width of 370fs and a repetition frequency of 100kHz, and the spectra of probe beam is recorded as a function of the delay between the pump and the probe beam. Given that our pump en-
TABLE II. Angle- and wavelength-dependent nonlinear refractive index $n_2$ and nonlinear absorption coefficient $\alpha_2$ and corresponding enhancement factors.

| $\lambda (\text{nm})$ | $\theta (^\circ)$ | $n_2$  | $\alpha_2$ | $n_2$ | $\alpha_2$ |
|-----------------------|------------------|--------|------------|--------|------------|
| 1300                  | 0                | 0.47   | -0.20      | 1      | 1          |
| 1800                  | 0                | 0.53   | -0.38      | 1.14   | 1.91       |
| 1550                  | 0                | 2.23   | -0.94      | 4.79   | 4.75       |
| 1550                  | 20               | 4.90   | -2.49      | 10.52  | 12.52      |
| 1550                  | 30               | 7.21   | -3.14      | 15.48  | 15.81      |
| 1550                  | 40               | 10.62  | -4.33      | 22.80  | 21.78      |

$^a$ $\lambda$, wavelength; $\theta$, angle of incidence; $n_2$, nonlinear refractive index with unit of $10^{-2} \text{cm}^2 \cdot \text{GW}^{-1}$; $\alpha_2$, nonlinear absorption coefficient with unit of $10^3 \text{cm} \cdot \text{GW}^{-1}$; enhancement factor is defined as the ratio between the corresponding value and the value at $\lambda = 1300\text{nm}$, $\theta = 0^\circ$.

Energy ($E_{\text{pump}} = 2.4\text{eV}$) is less than the bandgap of PEDOT ($E_g = 3.81\text{eV}$), the holes with energy higher than the Fermi level are pumped to the location below the Fermi energy level through intravalence band excitation and subsequently cooling down to the top of the valence band via electron phonon scattering (Fig. 3(g)). This physical picture is a mirror description of the excitation and relaxation of hot electrons in N-type ENZ materials. Although our excitation wavelengths are not located at ENZ wavelengths due to experimental constraints, the laser pulse still only excites the intraband transition and therefore can still provide evidence for optical nonlinearity enhancement caused by intraband-transition-induced hot carriers. Although there are complex local energy levels (polaron and bipolaron) in organics, we continue to use the excitation model of hot carriers to describe the transient processes in PEDOT for simplicity because the optical nonlinear enhancement due to hot carriers has been clearly investigated in a variety of inorganic ENZ materials.

signal response exhibits a "long-tail" characteristic, yet the model predicts a fast decay in the carrier temperature. However the bi-exponential model shows a very consistent fit to the measurement result. According to bi-exponential cooling dynamics[29], the relaxation rate depends on the lifespan of the optical phonon, and the strength of the optical to acoustic phonon interaction during the early and late stages of cooling, respectively. In the initial stage of cooling, the hot carriers lose energy by emitting optical phonons, and the electron-phonon coupling strength determines the decay rate. For our material, the time scale of ultrafast optical phonon emission is $\tau_{\text{OP}} = 0.35 \pm 0.022\text{ps}$. This is followed by a slow cooling of $\tau_{\text{OP} - \text{AP}} = 6.89 \pm 0.93\text{ps}$ from hot optical phonons to acoustic phonons, since the hot phonon is not able to cool quickly and thus re-heats the electron system. This effect is sometimes referred to as the hot phonon bottleneck for carrier cooling, which is limited by the coupling between the longitudinal optical phonon and the lattice[29–31]. Our two-temperature model consider only the heat dissipation process of hot carriers constricted by the strength of the electron-phonon coupling and ignore the heat dissipation of hot phonons in the material, thus exhibiting an inconsistency in the latter half.

Hot phonon bottleneck is typically observed in highly excited polar semiconductors, such as CdS, GaN, GaAs, and halide peroskites[31–33]; therefore, we speculate that the presence of hot phonon bottleneck in PEDOT: PSS is because the PSS component (a kind of polar group) leads to similar characteristics to polar semiconductors.

Comparative analysis between organic and inorganic ENZ materials

As a novel p-type organic ENZ material, it is essential to compare PEDOT to well researched inorganic ENZ materials, like indium tin oxide (ITO)[1]; gallium doped zinc oxide (GZO)[34], indium doped cadmium oxide (In: CdO)[8] and aluminum-doped zinc oxide (AZO)[12](Fig. 4(a)). PEDOT: PSS exhibit tolerable imaginary permitivity at ENZ wavelengths and can realize ENZ wavelengths from the near-infrared region to visible region which inorganic ENZ materials can hardly have. The modified PEDOT shows intrinsic optical nonlinear responses 100 times larger than those of ITO and basically equal to gold[35, 36], as given in the Fig. 4(c) and Supplementary Table. S1. This is attributed to the $\pi$-conjugated electron structure of PEDOT and the preferred molecular alignment. Here, the intrinsic optical nonlinear responses mean the $n_2$ and $\alpha_2$ outside of ENZ region and the ENZ optical nonlinear responses are the $n_2$ and $\alpha_2$ enhanced by hot carriers at ENZ wavelengths. However, the ENZ-induced optical nonlinear enhancement is weaker in PEDOT than in ITO, as shown in Fig. 4(c) and Fig. S3.
FIG. 4. The different ENZ features between organic and inorganic ENZ materials. (a) Comparison of semiconductor ENZ materials and the uniqueness of PEDOT as an ENZ material. The data of PEDOT is based on this work and our previously reported work[18]. (b) The transient responses of metallic PEDOT (P-type organic semiconductor ENZ material) and ITO (N-type inorganic semiconductor ENZ material). The time span \( \tau \) is defined as the time difference between two points equal to \( e^{-2} \) of the peak value. \( \tau_{\text{PEDOT}} = 1.46 \text{ps} \) and \( \tau_{\text{ITO}} = 0.65 \text{ps} \). Transient signals of ITO are adapted from M. Alam[1] with permission. (c) Comparative analysis between the nonlinearity enhancement factor produced by the ENZ effect of modified PEDOT and ITO[1]. The enhancement factor is defined as the ratio of \( n_2 \) (or \( \alpha_2 \)) in current situations (ENZ nonlinearity) to \( n_2 \) (or \( \alpha_2 \)) outside ENZ regions (intrinsic nonlinearity). Table II and Table. S1 contain detailed values. (d) The absorptance \( A \) of PEDOT and ITO as functions of wavelength and incident angle. The absorptance of ITO is calculated based on the permittivity reported by M. Alam[1].

According to coupled differential equations presented in the Supplementary Information, the nonlinearity enhancement is constrained by the elevated transient carrier temperature \( T_e \) after the arrival of the laser pulse. In Fig. S4, the peak values of free-carrier temperature \( T_e \) are displayed as functions of wavelength and incidence angle. The temperature profile demonstrates the primary characteristics shown in Fig. 3(e) and 3(f), namely an augmentation of the nonlinear response at ENZ wavelengths that increases with angle of incidence \( \theta \) between 0° and 40°. Equations in Supplementary Information indicates that the sample absorbance affects the energy absorbed by the sample and used to heat the electrons. Due to the sample’s equivalent complex refractive index \( N_{\text{eff}} = N / \cos(\theta) \) for TM polarization that varies drastically with wavelength and angle near the ENZ wavelength, the sample absorbance \( A \) that obeys Fresnel’s formula will depend heavily on the wavelength and angle of incidence, which is the origin of the enhanced nonlinearity of the ENZ material. Fig. 4(d) presents the difference in absorbance between PEDOT and ITO in the ENZ and non-ENZ regions, which perfectly explains that the nonlinear response \( n_2 \) and \( \alpha_2 \) in Fig. 4(c) and Fig. S3 is only enhanced by a factor of 22 for PEDOT but a factor of 2200 for ITO. Due to the hot phonon bottleneck exhibited in PEDOT, which is not present in conventional inorganic ENZ crystal materials, the relaxation time of the measured transient response signal is much longer than that of ITO[1] (\( \tau = 0.65 \text{ps} \), Al: ZnO[12] (\( \tau \approx 0.4 \text{ps} \)) and In: CdO[10] (\( \tau \approx 0.5 \text{ps} \)) (Fig. 4(d)). In a word, compared to inorganic semiconductor ENZ materials, organic ENZ materials have the following distinguishing characteristics: greater intrinsic nonlinearity due to \( \pi \)-conjugated structures, smaller enhancement factors due to large imaginary permittivity, and longer hot carrier relaxation time due to hot phonon bottlenecks.

Improvability of organic ENZ materials

Notably, the ENZ properties of our metallic PEDOT are based on good conductivity as well as heavy doping, and the conductivity of our PEDOT (961S/cm) is not very prominent compared to various other preparation methods (with a maximum of 6259S/cm). Various techniques, such as pre-treatment, post-treatment, changing the film formation method, embedding carbon nanotubes and silver nanowires into PEDOT[37–39], have been employed to further improve the electrical conductivity, resulting in the widespread replacement of ITO by PEDOT as a transparent electrode material in the field of flexible electronics. Therefore, numerous additional methods for preparing highly-conductive PEDOT films can be investigated in the future in turn to tune the ENZ wavelength more broadly, reduce optical losses, increase the enhancement factor, and produce distinct hot carriers behavior. Our previous reports[18] and this work demonstrate that PEDOT films with boosted electrical conductivity can have an ENZ wavelength from 600nm to 1550nm, which covers all bands (B, O, E, S, C, L, U band) in optical communications and a portion of the visible region where ITO is difficult to reach.

**CONCLUSION**

In summary, the modified PEDOT films treated with ethylene glycol exhibit features of P-type metallic polymers: high carrier concentration (10^{21} \text{cm}^{-3}), high hole mobility, Fermi level within the valence band and an ENZ wavelength of 1555nm. Due to \( \pi \)-delocalized electrons, the metallic PEDOT film exhibits intrinsic nonlinear optical responses (\( n_2 \) and \( \alpha_2 \)) 100 times larger than those of ITO and comparable to those of gold. The metallic PEDOT film finally achieves an ENZ-enhanced nonlinear refractive index up to the order of \( 10^{-14} \text{m}^2/\text{W} \) and nonlinear absorption coefficient up to \( 10^{-8} \text{m}/\text{W} \). Two-temperature model and the pump-probe measurement explain this ENZ-enhanced nonlinearity originates from the excita-
tion and relaxation of hot holes in PEDOT within the valence band. The hot phonon bottleneck of PEDOT prolongs the relaxation time of the hot holes, allowing the carriers to remain in the “hot” state for a longer duration. π-conjugated polymer ENZ materials not only exhibit different properties from inorganic ENZ materials, but also have great potential for further improvement. Thus, we believe that the unique advantages of PEDOT over ITO make it a strong competitor to ITO in nonlinear nanophotonic, nanophotonic, and plasmonic applications.

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