

Clarifying the origin of second-harmonic generation from an epsilon-near-zero film-coupled plasmonic nanoparticle-on-mirror system by size-dependence properties

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Abstract. We conduct a comprehensive numerical investigation on the size-dependence properties of second harmonic generation (SHG) from an epsilon-near-zero (ENZ) film-coupled plasmonic nanoparticle on-mirror (NPoM) system. The distinct size dependence of gold and indium-tin-oxide (ITO) leads to the existence of a critical point where the SHGs from these two materials are balanced. This study offers valuable guidance in the design of plasmonic systems containing ENZ materials for enhancing SHG.

Keywords: Second-harmonic generation / epsilon-near-zero / nanoparticle-on-mirror / size-dependence

1 Introduction

In the field of nanophotonics, plasmonic metasurfaces composed of nanoparticle-on-mirror (NPoM) structures have emerged as a subject of extensive research interest [1–3]. These NPoM systems support a strong plasmonic gap mode that highly confines the field in the ultrasmall nanocavity, leading to substantial field enhancement [3,4]. Remarkably, this system can be efficiently generated through a straightforward self-assembly process [5], resulting in a myriad of applications in diverse areas, including surface-enhanced Raman scattering (SERS) [6,7], enhanced photoluminescence [8], fluorescence enhancement [9], and nonlinear optics [10]. In the fabrication of NPoM system, a variety of materials have been chosen as spacer layers to separate nanoparticles (NPs) from films, encompassing polymers [9,11,12], metal oxides [13,14], and silicon dioxide [6,15].

Epsilon-near-zero (ENZ) materials, a novel and significant class of materials in nanophotonics, have garnered considerable attention in recent years [16–18]. ENZ materials exhibit a unique property where the real part of permittivity becomes zero at a specific wavelength known as the ENZ wavelength [19]. In particular, a giant field enhancement given by the ENZ mode can be generated at this distinctive wavelength [20]. The ENZ phenomenon has been observed in various materials, including metals [21], phononic materials [22,23], doped semiconductors [24–27], and metasurface [28,29], and is

significantly influenced by material thickness [30]. Notably, transparent conductive oxides like indium-tin-oxide (ITO) are common ENZ materials [31,32]. Due to their excellent photoelectric control capabilities, ITO thin films enable all-optical manipulation of light [33–35]. Moreover, they efficiently enhance nonlinear optical responses due to their substantial field enhancement and ease of achieving phase-matching conditions [36,37]. For instance, Alam et al. harnessed ITO films to attain a remarkable Kerr nonlinearity [38].

In recent years, there has been a growing trend of incorporating ENZ materials into metasurfaces with metal nanostructures to facilitate the coupling of ENZ modes with surface plasmon resonance modes of metals [39,40]. Coupling the gap mode of metal nanocavities with the ENZ mode has been experimentally demonstrated to enhance the SHG [41]. Deng et al. exploited the coupling of the ENZ mode from ITO with the plasmon resonance mode from metal nanoparticles to achieve a strong enhancement of second-harmonic generation (SHG) from a plasmonic meta surface [42]. This work further demonstrates the SHG from the metasurface mainly stems from the ITO nonlinearity, while the contribution from gold can be neglected. This claim further motivates us to explore how the nonlinearity between ITO and gold differs.

In this work, we investigate the SHG from a plasmonic NPoM system comprising gold nanowire arrays on a gold film with an ITO film serving as a spacer. Firstly, we present the theoretical model and computational methods employed in our study. Secondly, the SHGs from gold and ITO are characterized by studying their dependence on the

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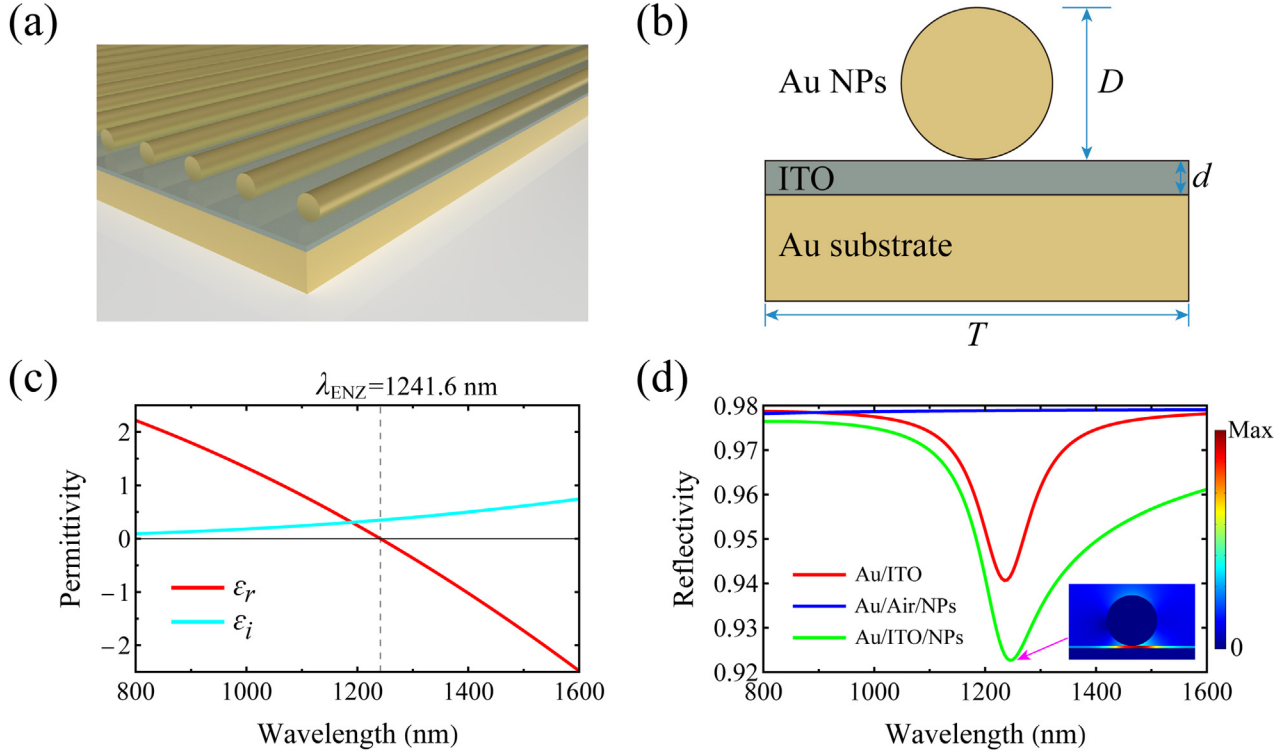


Fig. 1. (a) Schematic and (b) cross-section of the NPoM plasmonic system comprising a gold nanowire array supported by an ITO film on top of a gold substrate; (c) Real (red line) and imaginary (cyan line) parts of the ITO film described with the Drude model; (d) Reflectivity of a bare ITO film on a gold substrate (red line), a bare NPoM system (blue line), and an NPoM system with an ITO film as the spacer (green line), where the illustration shows the linear near-field intensity $|E|$ at the ENZ wavelength. For all three structural configurations, the period T is 100 nm, the ITO thickness d and air gap are 1 nm, and the nanoparticle diameter D is 20 nm. The angle of incidence is $\pi/4$.

geometric parameters, including the structural size and the thickness of the ITO layer. Our results confirm the existence of a critical point where the contributions from gold and ITO are balanced.

2 Theory model for SHG

At the beginning of the paper, we will introduce the model under investigation and the corresponding computational methods. The schematic diagram of the NPoM structure under investigation is presented in Figure 1a, with a cross-sectional view of one of the unit structures shown in Figure 1b. The NPoM system comprises an array of gold (Au) nanowires on a gold substrate, with an ITO thin film serving as the spacer layer. The symbols employed in our study include T for the structural period, D for the nanoparticle diameter, and d for the ITO film thickness. In this study, we characterize gold using the Drude model, $\varepsilon_{Au} = 1 - \frac{\omega_{p,Au}^2}{(\omega^2 + i\gamma_{Au}\omega)}$, with a plasma frequency of $\omega_{p,Au} = 1.36 \times 10^{16}$ rad/s and $\gamma_{Au} = 1 \times 10^{14}$ rad/s. ITO is also described by a Drude model $\varepsilon_{ITO} = \varepsilon_{\infty} - \frac{\omega_{p,ITO}^2}{(\omega^2 + i\gamma_{ITO}\omega)}$, with $\omega_{p,ITO} = 2.97 \times 10^{15}$ rad/s, $\gamma_{ITO} = 0.0468\omega_{p,ITO}$, and $\varepsilon_{\infty} = 3.8055$ [38], as shown in Figure 1c. The red and cyan lines in Figure 1c represent the real (ε_r) and the imaginary (ε_i) parts of ITO permittivity, respectively. According to the ENZ

condition, solving for $\varepsilon_r = 0$ yields the ENZ wavelength $\lambda_{ENZ} = 1241.6$ nm, as depicted by the dashed line in Figure 1c. With these material models, we employ the finite element method-based simulation software Comsol Multiphysics to investigate the light-matter interaction for the system shown in Figure 1b [43].

We have computed the linear optical response of various structural configurations, and the calculated reflectivity at an incident angle of $\pi/4$ is presented in Figure 1d. It is important to note that the selection of the angle here is merely to align with the angles used in the subsequent calculations of nonlinear responses. We have considered three configurations: (1) a 1 nm ITO film on a gold substrate (red line); (2) a bare NPoM system with a 1 nm gap (blue line); (3) a hybrid NPoM system with a 1 nm ITO film as the spacer (green line). In the case of a bare NPoM system, the reflection spectrum in the near-infrared (NIR) region exhibits a monotonic and weak variation. However, when introducing ITO as a spacer within the NPoM system, significant absorption enhancement occurs near the ENZ wavelength. Furthermore, the NPoM system with an ITO film displays stronger light absorption than an ITO film on a gold substrate. The absorption enhancement of the ITO film on a gold substrate can be attributed to the ENZ characteristics of ITO. However, as can be seen from the linear near-field intensity $|E|$ in Figure 1d, the enhancement in the NPoM system with an ITO film can be attributed to the coupling between the plasmonic gap mode and the ENZ mode.

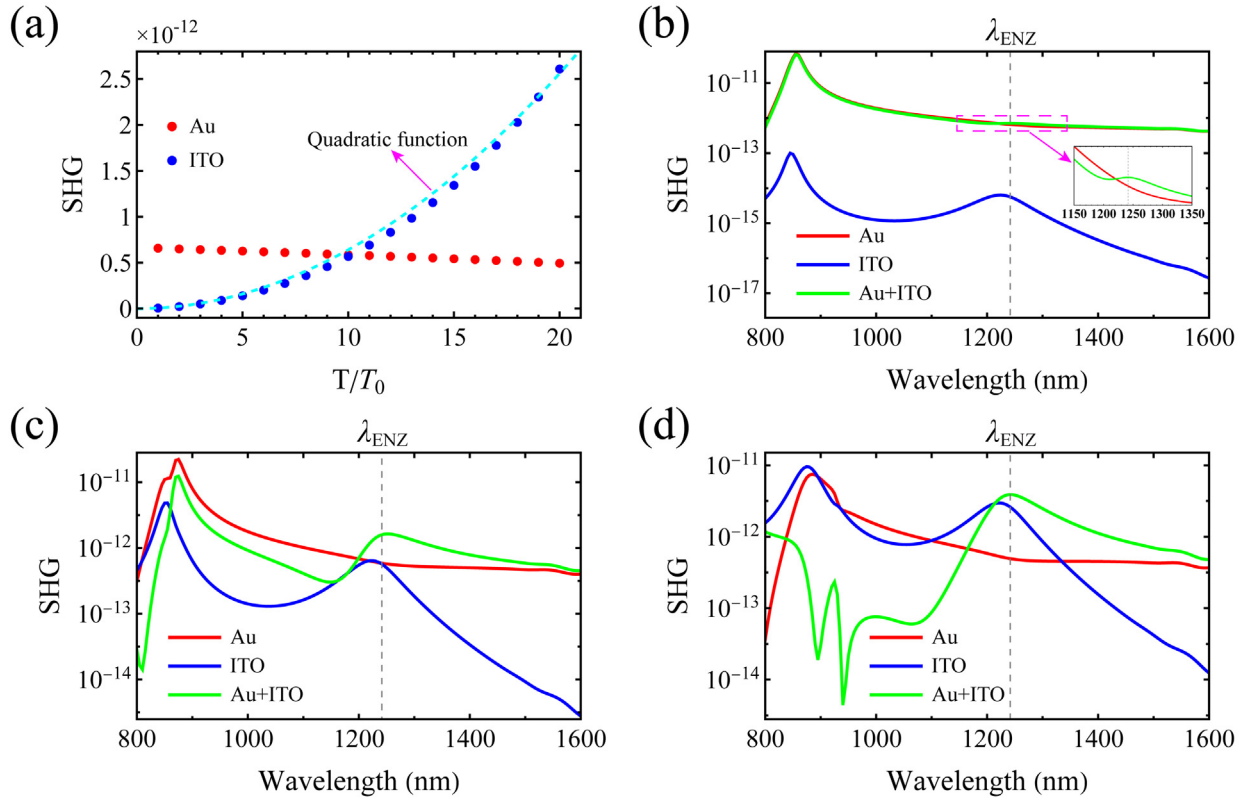


Fig. 2. Size-dependence study of SHG originating from gold and ITO. (a) SHG contributed by the gold (red dot) and ITO (blue dot) as a function as size parameter T where other geometric parameters change proportionally. Where the dashed cyan line represents a quadratic function with a coefficient of 6.4×10^{-15} . (b)–(d) SHG spectrum below/at/above the critical point. (b) $T = 10$ nm, $D = 2$ nm and $d = 0.1$ nm; (c) $T = 100$ nm, $D = 20$ nm and $d = 1$ nm; (d) $T = 200$ nm, $D = 40$ nm and $d = 2$ nm.

In our model, SHG arises from both the gold and ITO. For the gold NPoM, its contribution to SHG can be characterized by a pair of second-order nonlinear surface susceptibilities, as expressed by [44].

$$\chi_{\perp\perp\perp}^{(2)} = \frac{\varepsilon_0}{4} \frac{3\omega + i\gamma}{n_0 e 2\omega + i\gamma} (\varepsilon - 1)^2$$

$$\chi_{\parallel\perp\parallel}^{(2)} = \frac{\varepsilon_0}{2n_0 e} (\varepsilon - 1)^2, \quad (1)$$

where $\chi_{\perp\perp\perp}^{(2)}$ ($\chi_{\parallel\perp\parallel}^{(2)}$) is the components normal (parallel) to the metal surface, $n_0 = 5.7 \times 10^{28} \text{ m}^{-3}$ a typical equilibrium charge density of gold, and $-e$ is the electron charge. Since gold is a centrosymmetric medium, the second-order nonlinear process is forbidden in the bulk region, leading to the dominance of surface nonlinearity. Utilizing the surface nonlinear susceptibilities in equation (1), we derive the nonlinear surface polarizations $P_s^{(2)}$, which consist of two components, $P_{\perp}^{(2)} = \varepsilon_0 \chi_{\perp\perp\perp}^{(2)} E_{\perp}^2$ and $P_{\parallel}^{(2)} = \varepsilon_0 \chi_{\parallel\perp\parallel}^{(2)} E_{\perp} E_{\parallel}$, where ε_0 is the free space permittivity and $E_{\perp}$ ($E_{\parallel}$) denotes the normal (parallel) electric field at the metal interface, evaluated at the point immediately inside the metal. The induced surface polarization, acting as an excitation source, generates the nonlinear fields at the second-harmonic frequency. In addition, SHG from ITO is

described by a bulk second-order susceptibility $\chi_{zzz}^{(2)} = 1.8 \times 10^{-13} \text{ m/V}$, where z-axis is normal to ITO film [45]. This nonlinear susceptibility gives a polarization source field in the bulk of ITO film by $P_z^{NL} = \varepsilon_0 \chi_{zzz}^{(2)} E_z^2$.

Now, we have two origins for SHG: gold NPoM and ITO film. A comprehensive clarification and characterization of SHG from these two origins is presented in the next section. The detailed implementation in Comsol can be found in Appendix A.

3 Size dependence of SHG

In the previous section, we discussed the model of the ENZ-NPoM structure and the research methodology. In this section, we utilize this method to study the dependence of SHG from gold and ITO on the geometric parameters of the structure when pumped near ENZ wavelength. Due to the surface symmetry, for the excitation of SHG, the incident angle $\theta_{in} = \pi/4$ of the pump field is chosen as an example of oblique incidence throughout this paper.

We first study the size-dependence of SHG originating from gold and ITO separately, shown in Figure 2a. Here, we proportionally change the size of the structure with the shape unchanged. It is obvious that the SHG from gold and ITO follow different size dependencies, where SHG from gold is nearly size-independent, while that from ITO follows a quadratic function fitted with a dashed cyan line. The

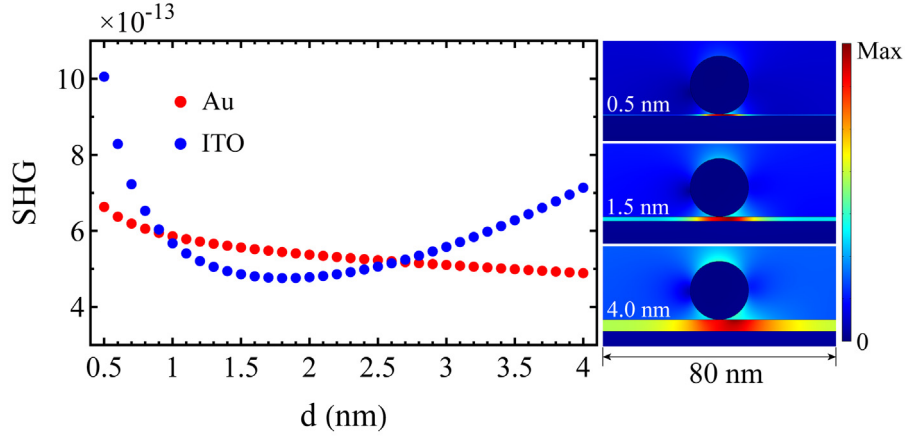


Fig. 3. The left side is SHG contributed by the gold (red dot) and ITO (blue dot) parts of the NPoM structure with different ITO thicknesses d , respectively. The right side presents the linear near-field intensity $|E|$ for ITO film thicknesses of 0.5 nm, 1.5 nm, and 4 nm.

interesting point is that a crossing point exists where the contributions from gold and ITO are balanced. At this critical point, the geometric parameters are $T = 100$ nm, $D = 20$ nm, and $d = 1$ nm. Below/Above this critical point, gold/ITO dominates the SHG process. Figures 2b–2d illustrate the SHG spectrum below, at, and above the critical point, respectively, which clearly confirmed the results in Figure 2a.

Let us first analyze the size-dependence of SHG from gold. The effective surface polarization, obtained by averaging the second-order nonlinear surface polarization over one period, is expressed as $\overline{P_{Au}^{(2)}} \propto \frac{1}{T} \int P_s^{(2)} dl$. In the quasi-static limit, the linear electric field is size-independent, thus making the nonlinear surface polarization $P_s^{(2)} \propto E^2$ size-independent. In addition, dl and T have the same size dependence. Therefore, the total surface polarization remains constant as the structure size proportionally changes. Consequently, SHG contributed by the gold is independent of structural size, as demonstrated in Figure 2a. Furthermore, it is noticeable that as the structure size increases, SHG from gold slightly decreases. This phenomenon is attributed to the breakdown of quasistatic approximation, where the retarded effect of electromagnetic waves comes into play.

The size dependence property of ITO film follows a quadratic relation with the size parameter. This dependence can be understood by analyzing the nonlinear polarization. The effective surface polarization can be obtained by averaging the bulk polarization inside ITO film over one period, and the relationship between them can be expressed as $\overline{P_{ITO}^{(2)}} \propto \frac{1}{T} \iint P_b^{(2)} dS$, where differential dS in the two-dimensional case is proportional to the square of size parameter. Similar to the surface polarization $P_s^{(2)}$ at the gold surface, the bulk polarization $P_b^{(2)}$ in the ITO is size-independent as a result of the electric field being size-independent. This relationship indicates that the effective surface polarization is proportional to the structural size. Consequently, SHG power from ITO follows a quadratic function of structural size, as illustrated in Figure 2a.

Figures 2b–2d display the second harmonic spectra for structural periods of $T = 10$ nm, 100 nm, and 200 nm, respectively. In each case, we calculated the SHG

contributed by gold (red line) and ITO (blue line), as well as their combined total (green line). The dashed line corresponds to the ENZ wavelength. These spectra demonstrate that we can only consider the SHG from the gold when the structure is a few tens of nanometers or even smaller. On the contrary, only SHG from ITO should be considered when the structure exceeds a few hundred nanometers, which further explains the dominance of ITO nonlinearity in Deng’s experimental work [42]. Furthermore, the SHG contribution from ITO is more sensitive to the ENZ condition, resulting in a resonance at the ENZ wavelength.

In the above, we have discussed the influence of structural size on SHG contributions from gold and ITO. Next, we explore how the ITO film thickness d affects SHG. For this analysis, we fix the structural parameters with a period of $T = 100$ nm and nanoparticle diameter of $D = 20$ nm. We calculate the SHG contributed by gold (red dots) and ITO (blue dots) at the ENZ wavelength for different ITO thicknesses ranging from 0.5 nm to 4 nm, as depicted in the dot plot on the left side of Figure 3. The right side of Figure 3 presents the linear near-field intensity $|E|$ for ITO film thicknesses of 0.5 nm, 1.5 nm, and 4 nm.

SHG from gold and ITO follow different dependencies on film thickness. The contribution from gold monotonically decreases when increasing the spacer thickness. In contrast, the SHG from ITO firstly decreases and then increases. These distinct behaviors can be understood with the near-field profile shown on the right panels. The electric field is strongly confined inside the gap region for a small thickness, generating large field enhancement when decreasing the gap size. It is this field enhancement mechanism that enlarges the SHG efficiency for both gold and ITO at a small gap size.

On the other hand, when increasing the ITO thickness, the field profile shows that the gap mode gets weakened, and the field becomes less confined, reducing the field enhancement. Therefore, the SHG from gold monotonically decreases. However, despite a reduced field enhancement, SHG from ITO rises as the film thickness increases for a relatively large gap (above 2 nm in Fig. 3). Increasing film thickness allows for the SHG process in a larger bulk ITO, which overwhelms the contribution from the field enhancement scenario.

The geometric dependence of SHG for our ENZ-NPoM hybrid system has been analyzed for a two-dimensional system. However, it applies to three-dimensional cases, such as periodic spherical nanoparticles on the mirror with an ENZ film as a spacer. Without loss of generality, we assume three-dimensional ENZ-NPoM has a square lattice with period T . For the nonlinear polarization of gold, $\overline{P_{gold}^{(2)}} = \frac{1}{T^2} \iint P_s^{(2)} dS \propto 1$, which is identical to the two-dimensional case. In contrast, the nonlinear polarization for ITO follows $\overline{P_{ITO}^{(2)}} = \frac{1}{T^2} \iint P_b^{(2)} dV \propto T$, the same as its two-dimensional counterpart as well.

4 Conclusion

In summary, we explore the size-dependent characteristics of SHG in a hybrid ENZ-NPoM plasmonic system. Our research highlights two crucial findings: firstly, SHG originating from gold is primarily associated with the gap mode, showing a weak dependence on the structural size. Conversely, SHG contributed by ITO arises from the coupling between the gap and ENZ modes, exhibiting a quadratic relationship with structural size. Secondly, we identify a critical size threshold determining whether gold or ITO plays a more substantial role in SHG from the hybrid ENZ-NPoM system. Furthermore, we examine the impact of ITO film thickness on the SHG and find the SHG from gold and ITO show different tendencies. Our comprehensive analysis unravels the intricate relationship between structural parameters and SHG contributions in hybrid ENZ-NPoM plasmonic systems, offering valuable insights for future nanophotonics and nonlinear optics applications.

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Conflicts of interest

The authors declare no competing interests.

Data availability statement

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

Author contribution statement

Conceptualization, F.Y.; Investigation, Y.Z.; Writing: Y.Z. and F.Y.; Supervision: F.Y. and F.G.

Appendix A: Comsol setup for SHG calculation

The numerical study for ENZ-NPoM hybrid structure is implemented in the finite element solver Comsol Multiphysics. The implementation of surface nonlinear polarization $P_{\perp}^{(2)}$ is straightforward because it can be related to a surface electric current. For the normal component of nonlinear surface polarization $P_{\perp}^{(2)}$, the weak form contribution is written as $\mu_0 \omega_S^2 \int_{\partial\Omega} P_{\perp} \tilde{\mathbf{E}} \cdot \hat{\mathbf{n}} dS$ where ω_S is the second-harmonic frequency, $\tilde{\mathbf{E}}$ is the test function, and integration is performed on the metal surface $\partial\Omega$ [46]. In contrast, the bulk nonlinear polarization inside the ITO layer can be implemented by the weak form contribution, $\mu_0 \omega_S^2 \int_{\Omega} \mathbf{P}_b \cdot \tilde{\mathbf{E}} dV$, where the integration is performed inside the ITO domain Ω .

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