

Non-reciprocal laser nano-structuring modulation via surface plasmon-polariton backscattering and spontaneous polarization synergy

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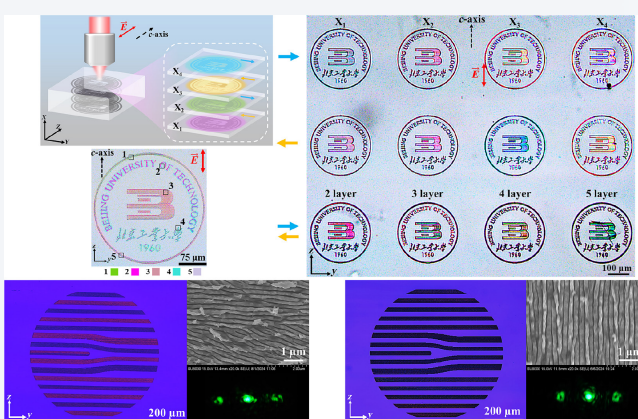
 **Cite this article:** *Nano Research*, 2026, 19, 94908885. <https://doi.org/10.26599/NR.2026.94908885>

ABSTRACT: The non-reciprocal (directional-dependent) nanostructuring phenomenon in birefringent crystals during ultrafast laser processing has long been considered an inherent limitation. Through systematic investigation of lithium niobate (LiNbO₃) surface nanostructuring, the synergistic interplay between surface plasmon-polariton (SPP) backscattering dynamics and the crystal's intrinsic spontaneous polarization field for the non-reciprocity of femtosecond laser nanostructuring in LiNbO₃ is demonstrated in this study. By strategically modulating laser polarization and scanning direction, the propagation of SPP can be well controlled, thereby enhancing the electric field via the interaction between SPP backscattering and spontaneous polarization, enabling amplification, suppression, and the complete removal of the non-reciprocal behavior of laser-induced periodic surface structures (LIPSS). Abundant phase modulations are achieved via only single laser polarized femtosecond laser irradiation on the LiNbO₃ by the modulation of non-reciprocal LIPSS, which successfully realizes different vortex beam distributions and depth-dependent pseudo-color nano-patterings. It provides a novel direct nanostructuring approach for LiNbO₃ with high controllability, efficiency, and uniformity via opposite laser writing and polarization adjustments, which is expected to enable advanced nano-optics devices, including optical data storage, shaping, and geometric phase optical elements.

KEYWORDS: non-reciprocal behavior, femtosecond laser, lithium niobate, nanostructuring

1 Introduction

Owing to the anisotropic crystal-induced difference in optical properties (refractive index, absorption, etc.), heterogeneous effects have been reported in the case of laser irradiation along various directions in anisotropic materials [1–3]. Optical non-reciprocity, as a phenomenon arising from broken time-reversal symmetry, leads to unequal transmission coefficients for opposite paths, such as



distinct transmission [4], scattering [5], or phase shifts [6] between forward and reverse propagation paths. For the ultrafast laser processing, the non-reciprocity resulting in the asymmetry of laser-induced micro/nano-structuring is further amplified, mostly leading to significant discrepancies in ablation or modification under opposite scanning directions [7–9]. Crucially, the presence of non-reciprocity introducing significant uncertainty due to laser processing dynamics in anisotropic crystals ultimately compromise the controllability of nanoscale fabrication [10, 11]. As one of the typical anisotropic crystals, lithium niobate (LiNbO₃) performs significant birefringence properties ($n_o - n_e \approx 0.07934$ at 1035 nm) [12]. It has been reported that the laser induced non-reciprocal modification of refractive index exists on *x*- or *y*-cut LiNbO₃ under the case of forward and reverse scanning parallel to the *c*-axis [13, 14]. The quill effect, a directional phenomenon observed even in homogeneous and isotropic materials, is well-established in

Received: February 28, 2026; **Revised:** May 25, 2026

Accepted: May 27, 2026

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dielectrics and metals [15, 16], its origin is interpreted in terms of pulse front tilt and/or pulse front asymmetry, which leads to a spatiotemporal asymmetry at the laser focus [17, 18]. Different from the reported “quill” effect, the non-reciprocal behavior in LiNbO₃ has been attributed to the co-effect of the photon drag behavior, light pressure, as well as the laser induced thermal currents caused by the anisotropic crystal structure, which exhibit strongly relation to the writing direction [19]. Recently, the interaction between the polarization and anisotropic crystal has gained great deal of attention since the polarization state may alter the intensity distribution and energy deposition near the focal volume, leading to variations in electron plasma generation [20], heat flow [21], and structural changes [22]. It has also been found that laser polarization can induce perturbations on the material bandgap and subsequently lead to the anisotropic ablation of LiNbO₃ [23]. The complex interaction between laser polarization and anisotropic crystal structure functioning on non-reciprocal machining behavior remains insufficiently explored, still requiring in-depth mechanistic understanding and systematic quantitative characterization.

Considering the subwavelength feature sizes and the adaptability to a wide variety of materials, laser-induced periodic surface structures (LIPSS) have emerged as a pivotal phenomenon and a versatile approach in nano-patterning, with broad applications across the fields of photonics, optoelectronics, and advanced material engineering [24, 25]. However, the deflection of LIPSS direction has been reported under various laser parameters, including polarization, scanning direction, laser power, while the LIPSS direction can be deflected up to 10° relative to the original angle, restricting the controllability in designed nano-patterning and large-area applications [26–28], such as optical data storage, polarization shaping, and the creation of geometric phase optical elements. The prevailing theory regarding LIPSS formation emphasizes the role of periodic energy deposition, primarily driven by the interference between the incident laser beam and waves scattered from the irradiated surface. These scattered waves include surface plasmon polaritons (SPPs) [29], surface electromagnetic waves [30], and other diffracted components [31] that contribute to ripple formation. In particular, upon the absorption of a high-intensity femtosecond pulse, the optical properties of a semiconductor or dielectric can be transiently altered to a metallic state due to the generation of a dense free electron plasma [24]. This transient metallicity enables the excitation of SPPs, which then interfere with the incident laser field, leading to a spatially modulated deposition of laser energy at the surface [32]. Under subsequent laser pulses, a positive feedback mechanism arises: the nascent periodic surface relief acts as a transient grating, resonantly assisting SPP excitation. The redshift of the SPP resonance frequency during this grating-assisted process further reduces the spatial period of the LIPSS, typically ranging from approximately 0.6λ to λ [33]. This SPP-based feedback mechanism successfully explains the formation of low-spatial-frequency LIPSS across a wide range of irradiation conditions. However, such interference-driven models are insufficient when the process is examined under laser-induced non-equilibrium states within multi-physics fields. These states encompass hydrodynamic motions [34], thermal quenching effects [35], and complex heat deposition/diffusion dynamics within the thermal field [36], all of which would introduce deviations from the ideal periodic structures, consequently causing significant misalignment in nano-patterns and leading to non-uniformity across large-area LIPSS [37, 38]. Non-reciprocal behaviors,

magnifying the deviations in the width, period, and orientation of LIPSS when scanned in opposite directions [39–41], should be more effectively controlled for the realization of desirable LIPSSs. These variations are attributed to factors such as the plasma resonance [39], the asymmetric focal spot during scanning [40], and half-periodic mismatched optical enhancement effect [41]. In contrast, the present study reveals an intrinsic non-reciprocal LIPSS behavior in LiNbO₃ that originates from the anisotropic crystal lattice itself, rather than from extrinsic pulse front asymmetry or a plasmonic feedback loop. How to avoid the non-uniformity of LIPSS due to non-reciprocal behavior is still ambiguous and receives little attention, limiting the fabrication of uniform LIPSS with long-range order in a large area, while the solving of this problem is significant for the design of highly controlled and reproducible nano-structuring for cutting-edge photonic devices and functional surfaces.

In this study, we demonstrate that the non-reciprocity is a tunable effect but not an inevitable limitation, which is governed by the synergistic coupling of SPP backscattering dynamics and the spontaneous polarization field. By strategically modulating laser polarization and scanning direction, the propagation of SPP can be well controlled, consequently leading to the electrical field enhancement via the interaction between SPP back scattering and spontaneous polarization, which can realize amplification, suppress, and entirely removing of the non-reciprocal behavior of LIPSS. The maximum LIPSS orientation modulation via non-reciprocity exceeding 25° by applying single polarization and suitable scanning direction. Leveraging this tunable non-reciprocity, it can govern the intrinsic symmetry-breaking arising from the relative angle between the laser polarization and the scanning direction, which can be applied for the multidimensional phase modulations through a single-polarization femtosecond laser irradiation. Programmable vortex beam generation and depth-encoded colorful nano-patterning with exceptional precision are realized via this innovative laser writing strategy, indicating new possibilities for the laser writing of nano-optics, particularly in ultrahigh-density optical data storage, structured light manipulation, and geometric phase metasurface fabrication without complex laser parameter modulation.

2 Experimental

As illustrated in Fig. S1 in the Electronic Supplementary Material (ESM), a femtosecond laser system (wavelength: 1035 nm, repetition rate: 750 kHz, pulse duration: 350 fs) is used for irradiation, with the laser beam focused through a 100× objective lens (numerical aperture: 0.7). A white light source is integrated into the same optical path as the laser beam through an optical coaxial system consisting of a beamsplitter (BS) and a dichroic mirror that reflects over 99.5% of the 1035 nm laser light. Polarization is adjusted by the half-wave plate (HWP) positioned before the focusing lens. The sample is mounted on a three-dimensional (XYZ) nano-positioning stage (ECSxy5050 series, Attocube Systems AG) with a travel range of 20 mm, a minimum step resolution of 10 nm, and a maximum speed of 4 mm/s. The stage's movements are automated using custom programming. The samples are a 5 mm × 5 mm × 0.5 mm *x*-cut LiNbO₃ crystal, as well as *x*-cut and *z*-cut thin film LiNbO₃ with sandwich structures including a 700 nm *x*-cut LiNbO₃ film (top), 2 μm silicon dioxide (middle), and a 330 μm silicon substrate (bottom). A charge-

coupled device (CCD) and a long working-distance objective lens are used to monitor the focal point and working distance in real-time from a top-down view. Scanning electron microscopy (SEM) images are captured using a Hitachi SU8000. Pseudo-color optical phase images are obtained using a polarizing microscope (Leica DM2700 P) combined with phase compensators and continuous laser irradiations at 532 nm.

3 Results and discussion

The non-reciprocal behavior is found in laser irradiation on *x*-cut thin film LiNbO₃ under two opposite scanning directions without changing laser polarization. In this study, the polarization is defined as θ . Here, $\theta = 0^\circ$ when the polarization is parallel to the *c*-axis, and $\theta = 90^\circ$ when the laser polarization direction is perpendicular to the *c*-axis. Femtosecond laser irradiates on the *x*-cut LiNbO₃ surface along the $\pm y$ directions with the laser polarization parallel and perpendicular compared with the *c*-axis, respectively. Two obvious irradiation areas with reversing scanning directions are created under orthogonal laser polarization, where the scanning speed and the laser fluence are 4 mm/s and 0.5 J/cm², respectively. For the polarization perpendicular to the *c*-axis, as shown in Fig. 1(a), the created lines exhibit similarly in both white light and pseudo-color images, meaning the laser fabrication is reciprocal under the two opposite scanning directions perpendicular to the *c*-axis of LiNbO₃, which is consistent with the reported work [7]. In another case, by only rotating the polarization to the direction parallel to the *c*-axis (*z*-direction) without changing other laser parameters, similarly no significant difference between the two reverse scanning lines under white light irradiation without modulation of the phase delay compensator (top image in Fig. 1(c)). However, an interesting phenomenon can be found that two lines with distinct pseudo-

colors of pink and blue are created by rotating the polarization parallel to the *c*-axis (bottom image in Fig. 1(c)), which is significantly different from the white light image. Since *x*-cut LiNbO₃ is a birefringent material and the line polarization interferes with the refracted light that passes through the material, the pseudo-color change indicates distinct phase modulations are realized via opposite laser writing. Various single-line scanning under different polarizations and opposite scanning directions are explored via further observation of SEM images. As shown in Figs. 1(b) and 1(d), the scanning directions in the experiment are along the *y* direction (orange arrow) and $-y$ direction (blue arrow), and the polarization angles are 0° and 90° ; the white dotted line means the *c*-axis. Here, the LIPSS angle is defined as φ , while $\varphi = 0^\circ$ when the LIPSS orientation is parallel to the *c*-axis. The φ is positive along anticlockwise rotation. The difference in the LIPSS orientation achieved by two opposite scanning directions is defined $\Delta\varphi$. In the case of $\theta = 90^\circ$ (Fig. 1(b)), the LIPSSs created by opposite directions show no distinct difference, while the direction of periodic nanostructures is perpendicular to the laser polarization ($\varphi = 0^\circ$). However, for the $\theta = 0^\circ$, despite the same polarization direction, the orientation of the LIPSS behaves with obvious deviations under the opposite scanning directions (Fig. 1(d)), as well as the difference between the two LIPSS directions is approximately $\Delta\varphi = 27^\circ$. The above SEM images illustrate that the pseudo-color optical phase difference characterized by the lines with opposite scanning directions (Fig. 1(c)) is due to the distinct deviation in LIPSS orientation.

To explore in detail the effect of incident polarization angles on the angular difference of LIPSS achieved by opposite scanning directions, statistics of LIPSS angle difference $\Delta\varphi$ vs. polarization angle θ under $\pm y$ directions scanning are plotted in Fig. 1(e) (see detail SEM images in Fig. S2 in the ESM). Obviously, at the range of

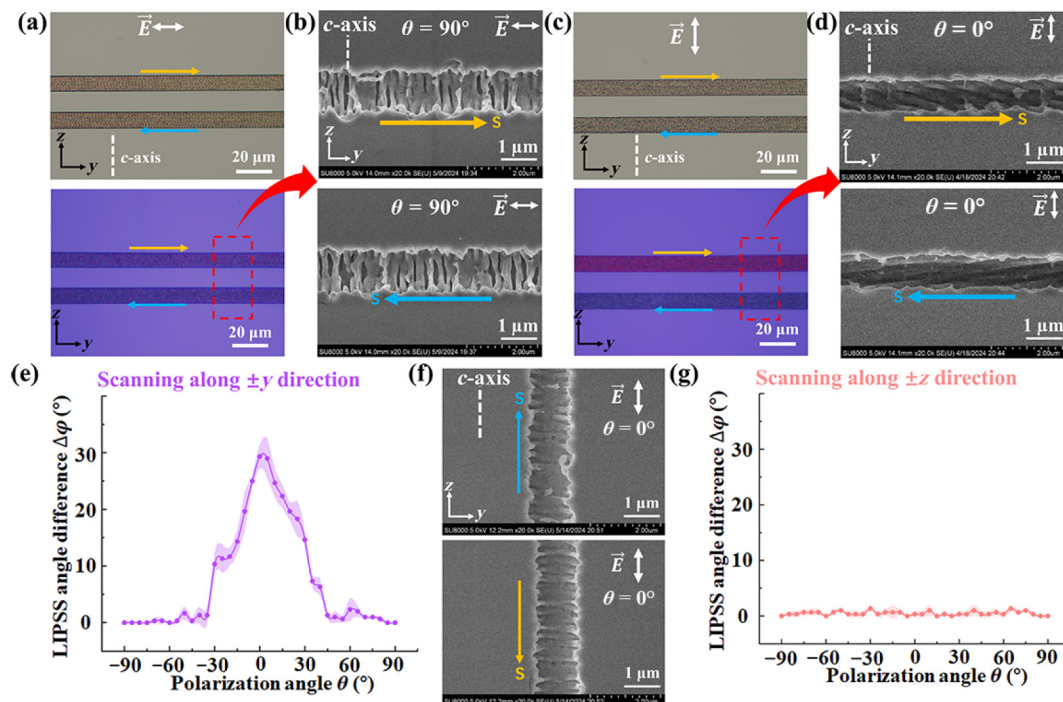


Figure 1 Non-reciprocal direct femtosecond laser writing on *x*-cut LiNbO₃ surface. White light and pseudo-color optical phase diagrams via phase compensator of direct writing in alternate scanning directions with polarization (a) perpendicular and (c) parallel to the *c*-axis. SEM images of laser direct writing LIPSS along two opposite directions and different laser polarization angles of (b) $\theta = 90^\circ$ and (d) $\theta = 0^\circ$. Statistical polarization angle θ vs. LIPSS angle difference $\Delta\varphi$ under (e) $\pm y$ directions and (g) $\pm z$ directions scanning. (f) SEM images of laser direct writing LIPSS along $\pm z$ directions at laser polarization angles of 0° .

$\theta = -30^\circ$ – 30° , the LIPSS angle difference $\Delta\phi$ formed by opposite scanning directions ($\pm y$ directions) shows significant non-reciprocity. However, for the polarization angle θ from $\pm 30^\circ$ – $\pm 90^\circ$, the nonreciprocity disappears completely, which is similar to the case of $\theta = 90^\circ$ (Fig. 1(b)). These results reveal a nonlinear relationship between the polarization angle and the non-reciprocal LIPSS orientations under $\pm y$ directions scanning, as well as the $\Delta\phi$ exhibits an axisymmetric distribution trend with c -axis ($\theta = 0^\circ$). However, in the case of $\pm z$ directions scanning, as shown in Fig. 1(f), the achieved LIPSSs exhibit reciprocal orientation. Furthermore, according to the statistics of LIPSS angle difference $\Delta\phi$ vs. polarization angle θ under $\pm z$ directions scanning is plotted in Fig. 1(g) (See detailed SEM images in Fig. S3 in the ESM), the LIPSS angle difference $\Delta\phi$ is lower than 2° , and no significant non-reciprocity is discovered on the LIPSS orientation under two opposite scanning directions along the c -axis. It means that the appearance of non-reciprocal behavior depends not only on the incident polarization direction but also on the scanning direction and the c -axis, revealing that non-reciprocal behaviors disappear in the case of polarization perpendicular to or scanning directions parallel to the c -axis, respectively. However, only two opposite scanning directions ($\pm y$ and $\pm z$ directions) have been discussed so far; the influence of scanning direction functioning on the non-

reciprocity of LIPSS orientation still requires further exploration under more cases of other opposite scanning directions.

Before the discussion on the influence of scanning direction for non-reciprocal LIPSS, the angle definition of scanning direction is plotted in Fig. 2(a). The angle between the scanning direction and the c -axis is α , while the value of α is positive in the case of counter-clockwise rotation. Here, each laser scanning line aims toward the central point, forming a radial pattern upon completion of the direct writing process. The interval angle between adjacent lines is set at 30° , and the lines are processed in opposite scanning directions, radiating outward from the pattern's center. Figure 2(b) exhibits the SEM images capturing the LIPSS on x -cut LiNbO₃ surfaces at polarization angle $\theta = 0^\circ$ and different scanning directions α . In the case of scanning angles $\alpha_1 = 90^\circ$ and $\alpha_2 = -90^\circ$, LIPSS angle difference $\Delta\phi$ is $\sim 23^\circ$. Similarly, for the opposite scanning direction pairs of $\alpha_1 = 0^\circ$ and $\alpha_2 = 180^\circ$, the LIPSS angles are $\sim 89^\circ$ and $\sim 91^\circ$, respectively, which is consistent with the above results shown in Fig. 1. Except for the above results, an interesting evolution law is found in other cases of scanning directions. For instance, the opposite scanning direction pairs of $\alpha_1 = 60^\circ$ and $\alpha_2 = -120^\circ$ can lead to LIPSS angles of 100° and 84° , exhibiting a $\Delta\phi = 100^\circ - 84^\circ = 16^\circ$. By changing α_1 to 30° and α_2 to -150° , the $\Delta\phi$ keeps decreasing to $95^\circ - 86^\circ = 11^\circ$, revealing that the $\Delta\phi$ will

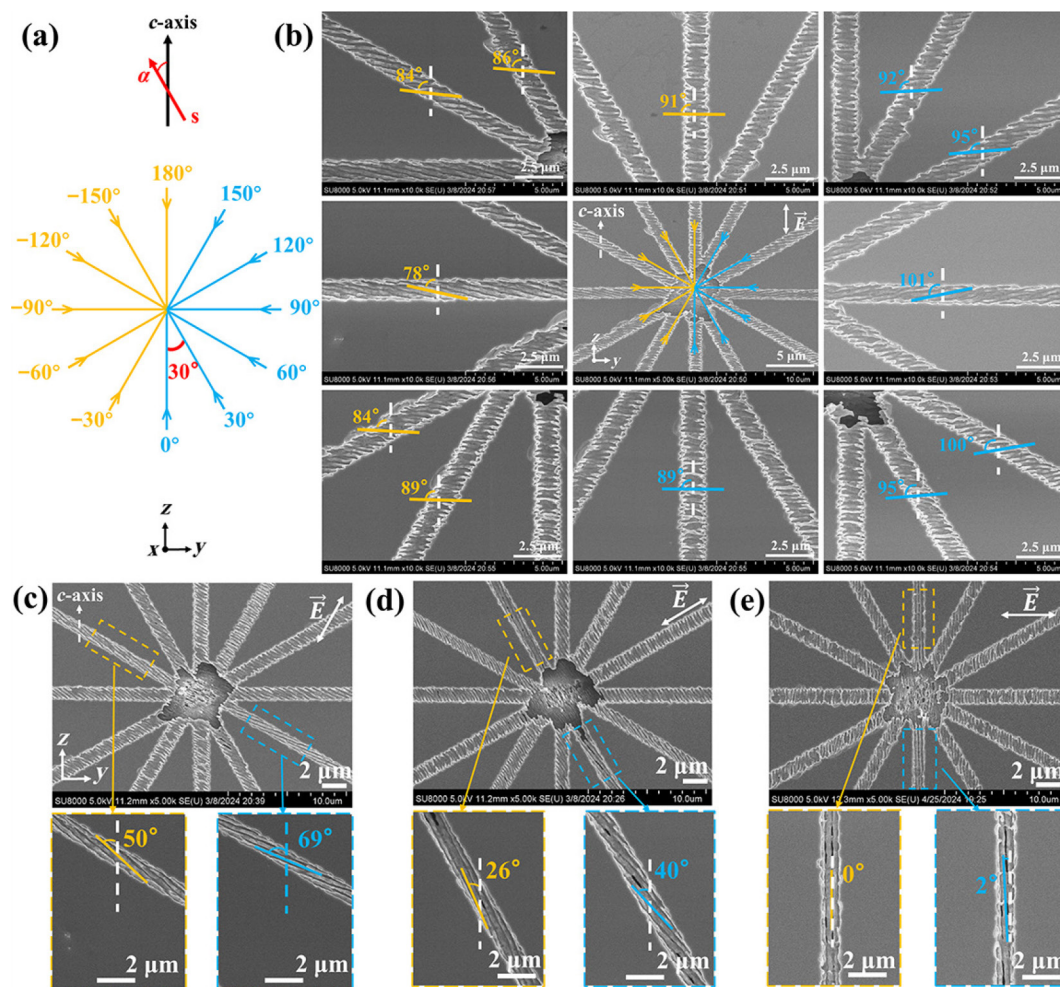


Figure 2 Non-reciprocal direct femtosecond laser writing on x -cut LiNbO₃ surface. Non-reciprocity of LIPSS fabricated at different scanning directions. (a) Schematic diagram of laser scanning directions. SEM images of LIPSS fabricated under different scanning directions at polarization angles of (b) $\theta = 0^\circ$, (c) $\theta = 30^\circ$, (d) $\theta = 60^\circ$, and (e) $\theta = 90^\circ$.

reduce while the pair of opposite scanning directions becomes more and more close to the c -axis. Consequently, in the case of polarization angle $\theta = 0^\circ$ (parallel to the c -axis), the more the scanning direction deviates from the crystal axis, the more obvious the non-reciprocity will be. According to the above experimental results, the influence of scanning direction and polarization on the non-reciprocity should be considered simultaneously. The SEM images of the LIPSS achieved under more cases of polarization angles $\theta = 30^\circ$, 60° , and 90° at different scanning directions are shown in Figs. 2(c)–2(e). It can be observed in Fig. 2(c) that similar non-reciprocal behavior can be observed while the polarization angle is increased to $\theta = 30^\circ$. At scanning angles $\alpha_1 = 60^\circ$ and $\alpha_2 = -120^\circ$ (perpendicular to the polarization), the LIPSS orientation behaves with obvious deviation, resulting in LIPSS angles of 69° at $\alpha_1 = 60^\circ$ and 50° at $\alpha_2 = -120^\circ$, respectively. The maximum $\Delta\varphi = 69^\circ - 50^\circ = 19^\circ$, which is slightly lower than the maximum $\Delta\varphi$ in the case of polarization angle $\theta = 0^\circ$ (maximum $\Delta\varphi = 23^\circ$). Similarly, the non-reciprocity gradually disappears along with the scanning direction getting closer to the c -axis, while the LIPSS orientations remain perpendicular to the polarization direction for other scanning angles, with a uniform LIPSS angle $\theta = \sim 60^\circ \pm 5^\circ$ (see detailed SEM images in Fig. S4 in the ESM). The non-reciprocal patterns still appear in Fig. 2(d) at a polarization angle of $\theta = 60^\circ$. Here, it is still evident that there is a noticeable difference with LIPSS angles of 43° at $\alpha_1 = 30^\circ$ and 23° at $\alpha_2 = -150^\circ$. The LIPSS angle $\theta = \sim 30^\circ \pm 5^\circ$ for other scanning angles, keeping perpendicular to the polarization direction (see detailed SEM images in Fig. S5 in the ESM). Interestingly, in the case of $\theta = 90^\circ$ (Fig. 2(e)), the LIPSS orientations for scanning angles $\alpha_1 = 0^\circ$ and $\alpha_2 = 180^\circ$ show slightly different. Remarkably, at $\alpha_1 = 0^\circ$, the LIPSS angle measures approximately 0° , while at $\alpha_2 = 180^\circ$, it measures around 2° . This difference should be considered as the experimental error. In polarization perpendicular to the c -axis ($\theta = 90^\circ$), the LIPSS orientation keeps reciprocity in any scanning angle α . Various orthogonal scanning and polarization combinations are further displayed in Fig. S6 in the ESM. Both the pseudo-color and SEM images confirm that the non-reciprocity gets weaker while the scanning direction is closer to the c -axis. Additionally, the reflection of surface structuring under different laser processing parameters (Fig. S7 in the ESM) are measured, while this difference in reflectivity between opposite propagation directions is a direct, quantitative manifestation of optical non reciprocity. The above relationship between the scanning direction and polarization angle significantly impacts the formation and orientation of LIPSS, confirming the directional dependence of these nanostructures.

To discuss the effect of laser fluence on the non-reciprocal behavior of LIPSS, reverse scanning under laser fluence reduction from 0.45 to 0.3 J/cm^2 has been processed with a 4 mm/s scanning speed. According to the experimental results shown in Fig. 3(a), only the ablation width reduces by decreasing the laser fluence, while the non-reciprocal behavior of LIPSS is almost unchanged, demonstrating that there is no threshold effect for the formation of non-reciprocal LIPSS. The influence of pulse number on non-reciprocal behavior is also analyzed. Since the non-reciprocal LIPSS was realized under scanning mode, the pulse number can be controlled by using different scanning speeds. Laser irradiations in the case of a polarization direction perpendicular to the c -axis and different scanning speeds are further explored while maintaining 0.5 J/cm^2 laser fluence. As shown in Fig. S8 in the ESM, apparent non-reciprocal LIPSS formation induced at different scanning

speeds (1 , 2 , and 4 mm/s , corresponding to the overlapping pulse numbers of 750 , 375 , and 187) can be observed, and the LIPSS difference between the opposite scanning direction is similar. Consequently, it can be confirmed that the pulse number does not significantly contribute to the formation of non-reciprocal LIPSS in orientation under opposite scanning. To further analyze the formation mechanism of non-reciprocal behavior, the opposite scanning process was decomposed into single, three-, and five-dot irradiations, respectively. For the case of three-dot, the first irradiation point is in the center, then move toward left and right $0.5 \mu\text{m}$ for the subsequent irradiation points, while the five-dot irradiations keep moving. The irradiation is conducted in situ using a dotting mode, with an exposure time of 1 ms per dot under 750 kHz repetition while each point with ~ 750 pulse irradiations. It can demonstrate the evolution that leads to non-reciprocal behavior through the point-point overlapping, as shown in Figs. 3(a)–3(c). It can create a typical LIPSS structure in the case of single dot irradiation (Fig. 3(a)). By extending the irradiation (still 750 laser pulses per dot) on the left and right from the single dot, as shown in Fig. 3(b), which is similar to the case of scanning mode as blue and orange arrows, respectively, it can be found that the orientation of LIPSS exhibits significantly difference ($\Delta\varphi = \sim 20^\circ$) on the two opposite extending sides. By further extending to five-dot irradiation (Fig. 3(c)), the orientation difference of LIPSS remains at $\Delta\varphi = \sim 20^\circ$. These irradiation results under different dots irradiation perform a similar LIPSS distribution to the non-reciprocal behavior achieved under scanning mode. In this case, there are no accumulation of thermal current between two dots irradiation, meaning the non-reciprocal behavior is not due to the thermal currents via non-equilibrium dynamic temperature [19].

The formation mechanism of non-reciprocal LIPSS is discussed via numerical calculations. The schematic diagram for the formation mechanism of non-reciprocal LIPSS is plotted in Fig. 4(a). First of all, as the concentration of conduction electrons increases after femtosecond laser irradiation (see calculated conduction electrons density in Fig. S9 in the ESM), the x -cut LiNbO_3 surface is gradually metallized and SPPs are excited [42, 43], resulting in a periodic energy deposition and creating typical LIPSS. With the scanning of femtosecond laser, the subsequent laser-induced SPPs backscatter and interact with the existing LIPSS cavity. Additionally, the intrinsic spontaneous polarization field of x -cut LiNbO_3 , which points along the c -axis ($+z$ axis), also interacts strongly with the backscattering SPPs, leading to the non-reciprocal behavior of LIPSS. Corresponding numerical simulations are calculated via a simplified model of single nano-line under the co-effect of backscattering SPPs and spontaneous polarization (see detailed setting of numerical simulations in Fig. S10 in the ESM). First, in the case of scanning direction along $\pm z$ -axis (parallel to the c -axis), as shown in Fig. 4(b), the enhancement of electrical field exhibits strong correlation to the incident polarization. The direction of enhanced electrical field is symmetrical under opposite scanning direction, which corresponds to the reciprocity of LIPSS shown in Fig. 1(g). It means the femtosecond laser nanostructuring is not affected by the spontaneous polarization of x -cut LiNbO_3 in this case. For the scanning along the $\pm y$ -axis (perpendicular to the c -axis), the electrical field distributions only enhance while the incident polarization angle is $< 30^\circ$ (Fig. 4(c)). In this case, the propagation of SPPs is perpendicular to the spontaneous polarization of LiNbO_3 , which leads to the interference of SPPs and the spontaneous

polarization field. Consequently, the enhancement of electrical field is not only affected by the interaction between the backscattering SPPs and the existing LIPSS, but also influenced by the spontaneous polarization of x -cut LiNbO_3 . It can be observed in Fig. 4(c) that the enhancement of such electrical fields exhibits a non-reciprocal behavior under opposite scanning directions, revealing that the non-reciprocity of LIPSS originates from the co-effect of backscattering SPPs and the spontaneous polarization fields of x -cut LiNbO_3 . Additionally, calculations for the interference of SPP and spontaneous under different scanning directions ($\alpha = 30^\circ$ – 60° and $\alpha = -120^\circ$ – -150°) and polarizations ($\theta = -30^\circ$ – -60°) are performed, as shown in Fig. S11 in the ESM. It can be observed that under the SPP propagation directions of $\alpha = 30^\circ$ – 60° and $\alpha = -120^\circ$ – -150° , the SPPs are not perpendicular to the spontaneous polarization of x -

cut LiNbO_3 , and still have an electric field component that interferes with the spontaneous polarization field. Consequently, the propagation of SPP can be well controlled by strategically modulating laser polarization and scanning direction, as well as resulting in the electrical field enhancement via the interaction between SPP back scattering and spontaneous polarization, which can amplify, suppress, and entirely remove the non-reciprocal behavior of LIPSS. In the absence of spontaneous polarization in LiNbO_3 (Fig. S12 in the ESM), backscattering SPP calculations show that when scanning along the $\pm y$ -axis, the direction of the enhanced electric field is symmetric, indicating that the nonreciprocity disappears without the involvement of spontaneous polarization. Similarly, symmetry is maintained under other scanning directions and polarizations, meaning that the nonreciprocity disappears in

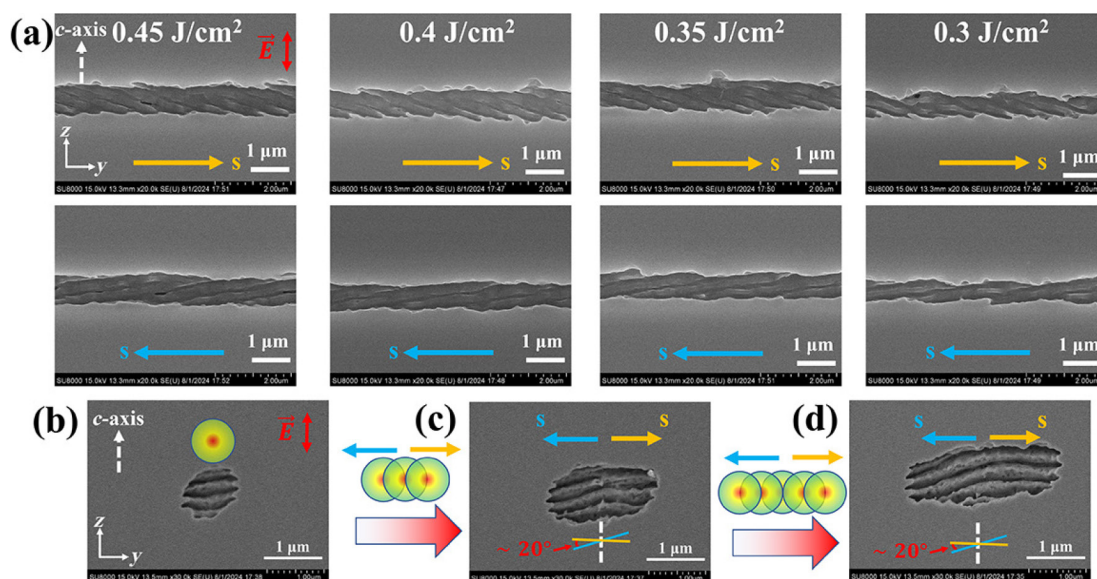


Figure 3 Non-reciprocal LIPSS realized under different processing parameters. (a) Non-reciprocal behavior at different laser fluences. The opposite scanning processes were reproduced by (b) single, (c) three, and (d) five-dot irradiations.

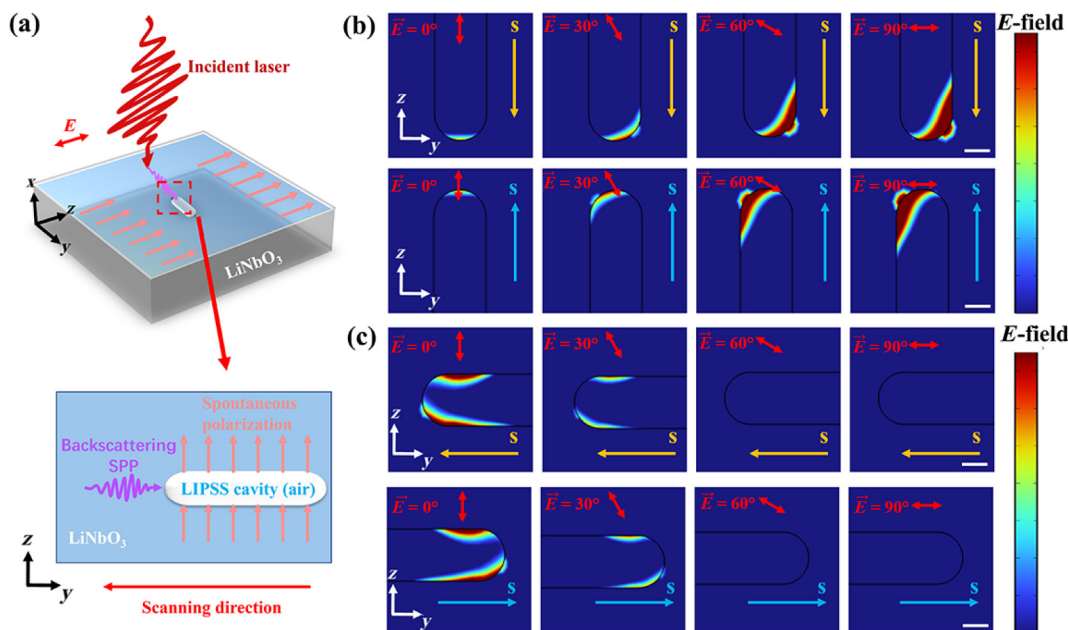


Figure 4 Formation mechanism of non-reciprocal LIPSS. (a) Schematic diagram for the co-effect of backscattering SPPs and spontaneous polarization. Corresponding electrical field distribution while the scanning directions are (b) parallel and (c) perpendicular to the c -axis. The SPPs are induced by the femtosecond laser with polarization angles of 0° , 30° , 60° , and 90° . The scale bar is 100 nm.

the absence of spontaneous polarization. Furthermore, the laser irradiation results of LIPSS on the *z*-cut LiNbO₃ are explored, as shown in Figs. S13 and S14 in the ESM. It can be observed that there is no obvious non-reciprocal behavior on the direction of LIPSS under the opposite scanning directions. Since the spontaneous polarization direction of *z*-cut LiNbO₃ is perpendicular to the surface (*x*-*y* plane), meaning there is interference between SPP backscattering and spontaneous polarization. Thus, the LIPSS keeps reciprocity in different polarization and scanning directions.

According to the above experimental results and mechanism analysis, the non-reciprocal behavior of LIPSS can be well controlled, which can be applied in large area nano-structuring with desirable patterns. However, the non-reciprocal behavior also occurs in the reported investigations of large-area LIPSS formation, leading to half-periodic misalignment of LIPSS and causing different types of original disorder [44]. Consequently, the influence of scanning spacing on the non-reciprocity of LIPSS should be first explored before the large area processing. As shown in Figs. 5(a) and 5(b), for 3 μm scanning spacing, there is no overlapping between the two reverse scanning nano-lines under the polarization direction of $\theta = 0^\circ$, laser fluence of 0.5 J/cm², and scanning speed of 4 mm/s. It can be observed that the angles between the direction of LIPSS and the *c*-axis (*z*-direction) are 70° and 95°, respectively, and there is a significant difference between the opposite scanning. By reducing the scanning space to 0.8 μm , the two scanning lines connect to each other, while the opposite LIPSS angles remain 70° and 95°, respectively. It indicates that the non-reciprocal behavior of LIPSS caused by opposite scanning directions (orange and blue arrows) is completely not affected by the overlapping of scanning space, meaning the applicability of non-reciprocal LIPSS in large-area laser nano-structuring. By modulating the non-reciprocity during large area processing of

LIPSS, orbital angular momentum (OAM) generators with different modulations are realized via the metasurface creation on *x*-cut LiNbO₃ crystal for the creation of ± 1 OAM beams. For the typical OAM generators, symmetric patterning is designed with the phase profile of 0 and π phase distribution, corresponding to the +1 and -1 OAM beams distributed in two opposite directions, resulting in two vortex beams with opposite OAM and equal intensity. A 532 nm fiber laser is applied for the generation of vortex beam via OAM generators, as shown in Fig. 5(c). In the first case (Fig. 5(d)), by introducing non-reciprocity into the creation of LIPSS, further phase modulation can be realized, as shown in Fig. 5(e). Here, two different phase patterns are created via opposite laser scanning without changing polarization ($\theta = 0^\circ$) during laser processing, increasing the processing efficiency significantly. In this case, the different patterns fabricated by opposite laser scanning realize two phase modulations and generate a separate vortex beam. By tuning the polarization, the non-reciprocity can be erased totally. Obvious vortex beams can be observed according to the achieved diffraction patterns shown in the right bottom images of Fig. 5(d). It is because the LIPSSs are created under reverse scanning direction with the polarization perpendicular to the *c*-axis ($\theta = 90^\circ$), ensuring all LIPSSs are reciprocal and keeping overall processing uniformity. It demonstrates a feasible and new way to achieve desirable phase modulation via the precise turning of non-reciprocal behavior with high uniformity and efficiency for the optical phase modulator.

Except for patterns on the *x*-cut LiNbO₃ surface, this strategy can also perform well in the highly customized chromatic patterns with arbitrary shapes via various spatial combinations. Owing to the transparency of *x*-cut LiNbO₃ and laser direct writing properties, our methods inherently support the patterning of the chromatic pixels distributed in three-dimensional (3D) space, extending the concept of frame printing from two-dimensional (2D) to 3D. As shown in Fig. 6(a), the laser beam is focused into *x*-cut LiNbO₃ at

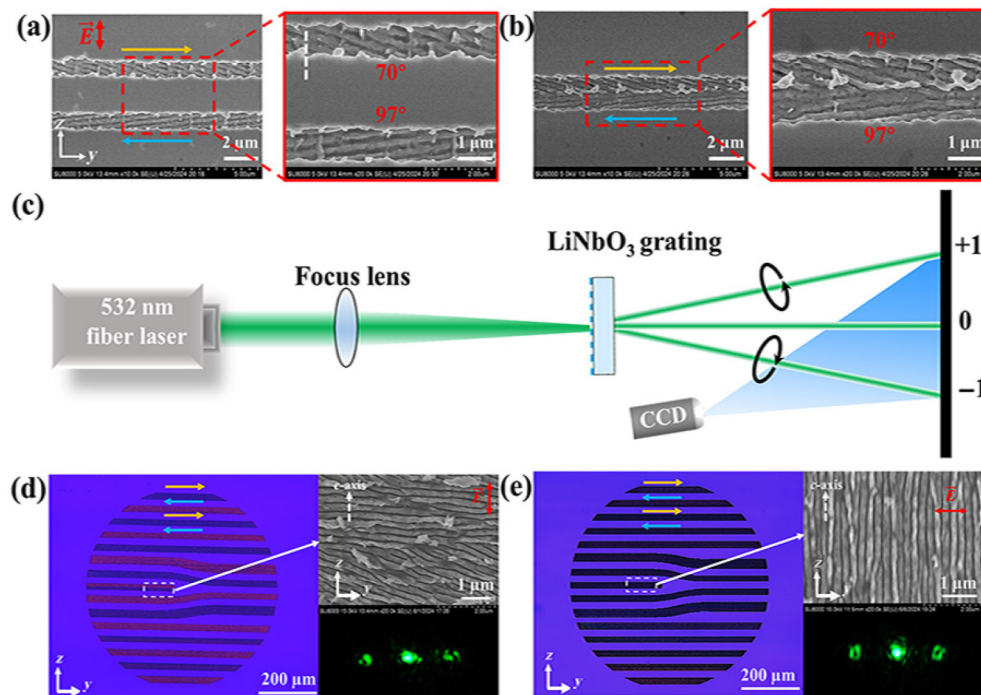


Figure 5 Application of non-reciprocal LIPSS direct writing on LiNbO₃ surface. SEM images of LIPSS created at different line spacings of (a) 0 and (b) $\sim 2 \mu\text{m}$. (c) Schematic diagram for the measurement of vortex beam via OAM generators. Pseudo-color optical phase images, SEM images, and achieved diffraction pattern created by (d) reciprocal LIPSS and (e) non-reciprocal LIPSS. The orange and blue arrows are the scanning directions.

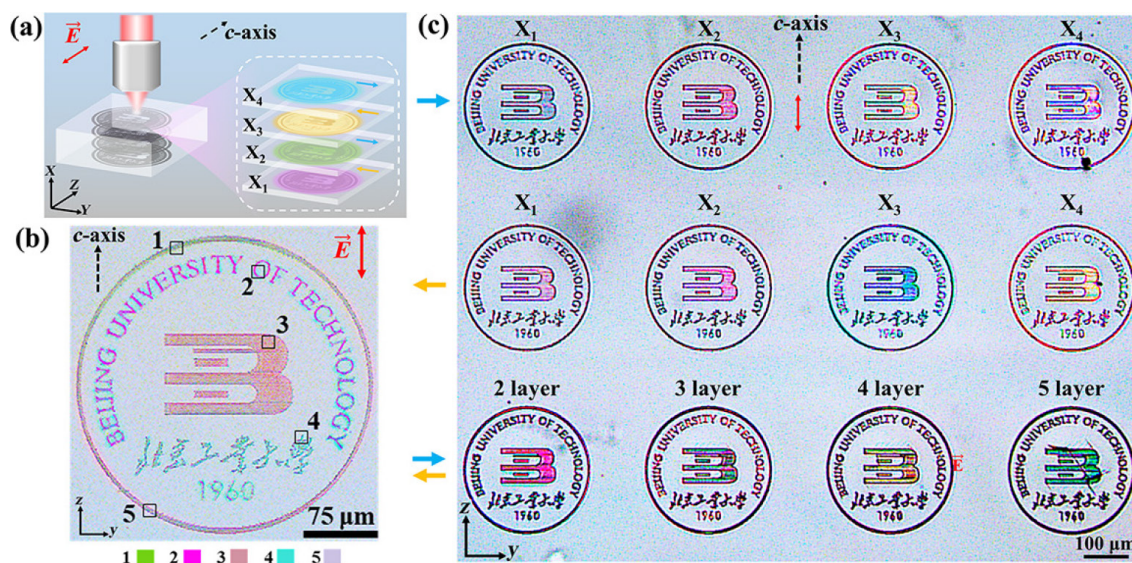


Figure 6 3D non-reciprocal direct writing inside x -cut LiNbO_3 crystal. (a) Schematic diagram of 3D non-reciprocal writing. (b) The optical phase coloring patterns of BJUT school badge via various combinations of scanning directions and focus depths. (c) Multiple coloring patterning of BJUT school badge.

different layers, while the X_1 , X_2 , X_3 , and X_4 mean the focus depths of 2, 4, 6, and 8 μm below the x -cut LiNbO_3 surface, respectively. As a proof of concept, customized patterns of BJUT school badges with multiple colors are created. Propagation of electromagnetic waves in such LIPSSs can consequently be described by the effective refractive indices originating from the effective-medium theory [45]. In this case, the electric field waves through the periodic nano-structures in different orientations possess a different amount of phase shift. As a result, the phase retardation (ψ) of transmitted light can be directly defined by the thickness (d) of the periodic nano-structures and the effective refractive index can be modulated ($\Delta n = n_{\text{TE}} - n_{\text{TM}}$) [45, 46], where $\psi = d \cdot \Delta n$. Consequently, compared to the LIPSS in single direction, the hybrid LIPSS can exhibit a diverse optical property due to the spatially varying phase shifts contributed by its multi-orientation nano-structure. According to the processing parameters of such baseline single-colors, a BJUT school badge with more than five colors is achieved via reasonable design, as depicted in Fig. 6(b). Consequently, different colors can be observed by using a polarizing microscope combined with a phase delay plate. As shown in Fig. 6(c), abundant color patterns are realized via the flexible use of non-reciprocal LIPSS controllability in three modes: positive scanning, reverse scanning, and hybrid layer scanning. Unlike traditional processing, the focus depth (2, 4, 6, and 8 μm below the x -cut LiNbO_3 surface) and scanning direction (positive and reverse scanning) can lead to eight various single-color patterns. Through the hybrid layer scanning (2–5 layers), four more single-color patterns are created. It should be noticed that all the above colors can be realized by using only one polarization ($\theta = 0^\circ$), which can significantly simplify and speed up the printing process of chromatic patterns in transparent media without changing polarization in real time laser processing, opening possibilities for LIPSS to play a role in emerging technologies such as optical storage and encryption.

4 Conclusions

In summary, we have fundamentally elucidated the origin of non-reciprocal nanostructuring in birefringent LiNbO_3 crystals during ultrafast laser processing. Through systematic investigations, the

directional-dependent behavior of LIPSS arising from the synergistic coupling between SPP backscattering dynamics and the crystal's intrinsic spontaneous polarization field is demonstrated. By strategically modulating the laser polarization and scanning direction, the propagation of SPP can be precisely controlled. This allows for effective modulation of the electric field enhancement resulting from the interaction between SPP back-scattering and the material's spontaneous polarization, which can amplify, suppress, or even entirely eliminate the non-reciprocal behavior in LIPSS. Exploiting this directional control mechanism, we further realized direct phase modulation on LiNbO_3 surfaces through single-polarization femtosecond laser irradiation, enabling vortex beam generation and depth-resolved pseudo-color nanopatterning. This strategy integrates polarization rotation with directional scanning, which transcends conventional fabrication limits and opens avenues for advanced nano-optics applications in high-density optical data storage, structured light devices, and geometric phase metasurfaces.

Electronic Supplementary Material: Supplementary material (experimental details and characterization data: SEM, reflectance spectra, calculated conduction electron density, numerical calculation setting, and calculations of electrical field) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908885>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work was granted by National Natural Science Foundation of China (Nos. 51975017 and 52405448) and the National Key Research and Development Program of China (No. 2018YFB1107500).

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

L. F. J.: Conceptualization, project administration, validation, investigation, funding acquisition, writing – original draft. B. H. Z.: Data curation, investigation, software, writing – original draft. Z. Y. L.: Conceptualization, software, investigation, writing – original draft. D. C. Y.: Conceptualization, project administration. W. G. S.: Data curation, software. T. N. Z.: Data curation. F. Y.: Data curation.

Use of AI statement

None.

References

- [1] Dąbrowski, M.; Haldar, S.; Khan, S.; Keatley, P. S.; Sagkovits, D.; Xue, Z. K.; Freeman, C.; Verzhbitskiy, I.; Griep, T.; Atxitia, U. et al. Ultrafast thermo-optical control of spins in a 2D van der Waals semiconductor. *Nat. Commun.* **2025**, *16*, 2797.
- [2] Zhang, B.; Yan, W. C.; Chen, F. Recent advances in femtosecond laser direct writing of three-dimensional periodic photonic structures in transparent materials. *Adv. Photonics* **2025**, *7*, 034002.
- [3] Zhou, Y. Y.; Wang, Y.; Zhang, K.; Leng, H. Q.; Müller-Buschbaum, P.; Li, N.; Qiao, L. Advanced applications of pulsed laser deposition in electrocatalysts for hydrogen-electric conversion systems. *Opto-Electron. Adv.* **2025**, *8*, 250096.
- [4] Zarif, A.; Jamshidi, K. Non-reciprocity in a silicon photonic ring resonator with time-modulated regions. *Opt. Express* **2024**, *32*, 26938–26953.
- [5] Pedernana, T.; Faure-Beaulieu, A.; Fleury, R.; Noiray, N. Loss-compensated non-reciprocal scattering based on synchronization. *Nat. Commun.* **2024**, *15*, 7436.
- [6] Shen, Z.; Zhang, Y. L.; Chen, Y.; Zou, C. L.; Xiao, Y. F.; Zou, X. B.; Sun, F. W.; Guo, G. C.; Dong, C. H. Experimental realization of optomechanically induced non-reciprocity. *Nat. Photonics* **2016**, *10*, 657–661.
- [7] Song, H.; Dai, Y.; Song, J.; Ma, H. L.; Yan, X. N.; Ma, G. H. Femtosecond laser-induced structural difference in fused silica with a non-reciprocal writing process. *Appl. Phys. A* **2017**, *123*, 255.
- [8] Guan, J.; Liu, X.; Booth, M. J. Ultrafast laser writing quill effect in low loss waveguide fabrication regime. *Opt. Express* **2018**, *26*, 30716–30723.
- [9] Tang, X. L.; Li, Y. D.; Sun, Y.; Zhai, Q. X.; Ma, H. L.; Dai, Y. Temporally chirped femtosecond pulse laser non-reciprocal writing on the silicon. *Appl. Phys. A* **2021**, *127*, 135.
- [10] Gao, L.; Zhang, Q. M.; Gu, M. Femtosecond laser micro/nano processing: From fundamental to applications. *Int. J. Extrem. Manuf.* **2025**, *7*, 022010.
- [11] Wanie, V.; Bloch, E.; Månsson, E. P.; Colaizzi, L.; Ryabchuk, S.; Saraswathula, K.; F. Ordonez, A. F.; Ayuso, D.; Smirnova, O.; Trabattini, A. et al. Capturing electron-driven chiral dynamics in UV-excited molecules. *Nature* **2024**, *630*, 101–115.
- [12] Labbé, F.; Ekici, Ç.; Zhdanov, I.; Muthali, A. L.; Oxenløwe, L. K.; Ding, Y. H. Thin-film lithium niobate quantum photonics: Review and perspectives. *Adv. Photonics* **2025**, *7*, 044002.
- [13] Xu, X. Y.; Wang, T. X.; Chen, P. C.; Zhou, C.; Ma, J. N.; Wei, D. Z.; Wang, H. J.; Niu, B.; Fang, X. Y.; Wu, D. et al. Femtosecond laser writing of lithium niobate ferroelectric nanodomains. *Nature* **2022**, *609*, 496–501.
- [14] Wanie, V.; Shao, T. J.; Lassonde, P.; Ibrahim, H.; Deschamps, J.; Liu, J. Q.; Vargas, F. A.; Vidal, F.; Ruediger, A.; Calegari, F. et al. Control of strong-field ionization in ferroelectric lithium niobate: Role of the spontaneous polarization. *Phys. Rev. B* **2020**, *101*, 184103.
- [15] Kazansky, P. G.; Beresna, M. Quill and nonreciprocal ultrafast laser writing. In *Femtosecond Laser Micromachining*. Osellame, R.; Cerullo, G.; Ramponi, R., Eds.; Topics in Applied Physics: Berlin, 2012; pp 127–151.
- [16] Fuentes-Edfuf, Y.; Sánchez-Gil, J. A.; Garcia-Pardo, M.; Serna, R.; Tsibidis, G. D.; Giannini, V.; Solis, J.; Siegel, J. Tuning the period of femtosecond laser induced surface structures in steel: From angled incidence to quill writing. *Appl. Surf. Sci.* **2019**, *493*, 948–955.
- [17] Patel, A.; Svirko, Y.; Durfee, C.; Kazansky, P. G. Direct writing with tilted-front femtosecond pulses. *Sci. Rep.* **2017**, *7*, 12928.
- [18] Salter, P. S.; Simmonds, R. D.; Booth, M. J. Adaptive control of pulse front tilt, the quill effect, and directional ultrafast laser writing. In *Proceedings of the SPIE 8611, Frontiers in Ultrafast Optics: Biomedical, Scientific, and Industrial Applications XIII*, San Francisco, USA, 2013; pp 861111.
- [19] Yang, W. J.; Kazansky, P. G.; Svirko, Y. P. Non-reciprocal ultrafast laser writing. *Nat. Photonics* **2008**, *2*, 99–104.
- [20] Hu, K.; Yi, L. Q. Generation of isolated subfemtosecond electron bunches by the diffraction of a polarization-tailored intense laser beam. *Phys. Rev. Lett.* **2024**, *133*, 045001.
- [21] Ortiz-Rivero, E.; González-Gómez, C. D.; Rica, R. A.; Haro-González, P. Effect of the photoexcitation wavelength and polarization on the generated heat by a Nd-doped microspinner at the microscale. *Small* **2024**, *20*, 2308534.
- [22] Wang, Y.; Li, Z. Z.; Zhou, H. W.; Li, R. F.; Huang, J. T.; Lin, Z.; Chen, Q. D.; Wang, L.; Sun, H. B. Optical self-assembly of chiral nanostructures by a seed symmetry-breaking effect. *Laser Photonics Rev.* **2025**, *19*, 2402108.
- [23] Lin, Z. Y.; Ji, L. F.; Zhou, B. H.; Sun, W. G.; Yang, D. C.; Yang, F.; Yao, T. R. Energy band structure perturbation induced deviation on precise ultrafast laser nano-structuring. *Mater. Today Phys.* **2025**, *51*, 101636.
- [24] Han, R. Z.; Zhang, Y. C.; Jiang, Q. L.; Chen, L.; Cao, K. Q.; Zhang, S. A.; Feng, D. H.; Sun, Z. R.; Jia, T. Q. Ultrafast dynamics of femtosecond laser-induced high spatial frequency periodic structures on silicon surfaces. *Opto-Electron. Sci.* **2024**, *3*, 230013.
- [25] Yin, J. B.; Lin, Z. Y.; Ji, L. F.; Hong, M. H. Femtosecond laser micro/nano-processing via multiple pulses incubation. *Opto-Electron. Technol.* **2025**, *1*, 250003.
- [26] Ren, Y. Y.; Luo, S. L.; An, P.; Zhao, L. N.; Cai, Y. J.; Li, Z. Laser-induced periodic surface structures on Fe ion doped LN crystal for pyroelectric SERS analysis. *Appl. Phys. Lett.* **2024**, *125*, 031109.
- [27] Borodaenko, Y.; Pavlov, D.; Cherepakhin, A.; Mitsai, E.; Pilnik, A.; Syubaev, S.; Gurbatov, S. O.; Modin, E.; Porfirev, A. P.; Khonina, S. N. et al. Liquid-assisted laser nanotexturing of silicon: Onset of hydrodynamic processes regulated by laser-induced periodic surface structures. *Adv. Mater. Technol.* **2024**, *9*, 2301567.
- [28] Ni, J. C.; Huang, C.; Zhou, L. M.; Gu, M.; Song, Q. H.; Kivshar, Y.; Qiu, C. W. Multidimensional phase singularities in nanophotonics. *Science* **2021**, *374*, eabj0039.
- [29] Huang, M.; Zhao, F. L.; Cheng, Y.; Xu, N. S.; Xu, Z. Z. Origin of laser-induced near-subwavelength ripples: Interference between surface plasmons and incident laser. *ACS Nano* **2009**, *3*, 4062–4070.
- [30] Kim, B.; Nam, H. K.; Ryu, J.; Kim, Y. J.; Kim, S. W. Non-periodic nanoscale structuring of crystalline silicon surface by using ultrashort laser pulses. *Appl. Surf. Sci.* **2021**, *565*, 150595.
- [31] Zhang, H.; Colombier, J. P.; Li, C.; Faure, N.; Cheng, G. H.; Stoian, R. Coherence in ultrafast laser-induced periodic surface structures. *Phys. Rev. B* **2015**, *92*, 174109.

- [32] Bonse, J.; Rosenfeld, A.; Krüger, J. Implications of transient changes of optical and surface properties of solids during femtosecond laser pulse irradiation to the formation of laser-induced periodic surface structures. *Appl. Surf. Sci.* **2011**, *257*, 5420–5423.
- [33] Bonse, J.; Krüger, J.; Höhm, S.; Rosenfeld, A. Femtosecond laser-induced periodic surface structures. *J. Laser Appl.* **2012**, *24*, 042006.
- [34] Fraggelakis, F.; Tsiibidis, G. D.; Stratakis, E. Ultrashort pulsed laser induced complex surface structures generated by tailoring the melt hydrodynamics. *Opto-Electron. Adv.* **2022**, *5*, 210052.
- [35] Nakhoul, A.; Colombier, J. P. Beyond the microscale: Advances in surface nanopatterning by laser-driven self-organization. *Laser Photonics Rev.* **2024**, *18*, 2300991.
- [36] Alvarez-Alegria, M.; Ruiz de Galarreta, C.; Siegel, J. Real-time 3D Visualization of the formation of micrograting structures upon direct laser interference patterning of Ge. *Laser Photon. Rev.* **2023**, *17*, 2300145.
- [37] Öktem, B.; Pavlov, I.; Ilday, S.; Kalaycıoğlu, H.; Rybak, A.; Yavaş, S.; Erdoğan, M.; Ilday, F. Ö. Nonlinear laser lithography for indefinitely large-area nanostructuring with femtosecond pulses. *Nat. Photonics* **2013**, *7*, 897–901.
- [38] Geng, J.; Xu, L. Y.; Yan, W.; Shi, L. P.; Qiu, M. High-speed laser writing of structural colors for full-color inkless printing. *Nat. Commun.* **2023**, *14*, 565.
- [39] Kazenwadel, D.; Neathery, N.; Baum, P. Canalized light creates directional and switchable surface structures in vanadium dioxide. *Nat. Commun.* **2025**, *16*, 3960.
- [40] Nathala, C. S. R.; Ajami, A.; Ionin, A. A.; Kudryashov, S. I.; Makarov, S. V.; Ganz, T.; Assion, A.; Husinsky, W. Experimental study of Fs-laser induced sub-100-nm periodic surface structures on titanium. *Opt. Express* **2015**, *23*, 5915–5929.
- [41] Xu, Y. S.; Li, Z. Z.; Wang, Z. H.; Xia, H.; Liu, Y. F.; Juodkazis, S.; Chen, Q. D.; Wang, L. Nanoscale control of non-reciprocal ripple writing. *Opt. Express* **2023**, *31*, 14796–14807.
- [42] Huang, J. X.; Xu, K.; Xu, S. L.; Li, X. W.; Wei, Q. H. Self-Aligned Laser-induced periodic surface structures for large-area controllable nanopatterning. *Laser Photonics Rev.* **2022**, *16*, 2200093.
- [43] Li, Z. X.; Wu, Q.; Jiang, X. D.; Zhou, X.; Liu, Y. Y.; Hu, X. Y.; Zhang, J. M.; Yao, J. H.; Xu, J. J. Formation mechanism of high spatial frequency laser-induced periodic surface structures and experimental support. *Appl. Surf. Sci.* **2022**, *580*, 152107.
- [44] Yang, M.; Wu, Q.; Chen, Z. D.; Zhang, B.; Tang, B. Q.; Yao, J. H.; Drevensek-Olenik, I.; Xu, J. J. Generation and erasure of femtosecond laser-induced periodic surface structures on nanoparticle-covered silicon by a single laser pulse. *Opt. Lett.* **2014**, *39*, 343–346.
- [45] Yariv, A.; Yeh, P. *Optical Waves in Crystals: Propagation and Control of Laser Radiation*; Wiley: New York, 2002.
- [46] Cerkauskaite, A.; Drevinskas, R.; Solodar, A.; Abdulhalim, I.; Kazansky, P. G. Form-birefringence in ITO thin films engineered by ultrafast laser nanostructuring. *ACS Photonics* **2017**, *4*, 2944–2951.



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