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A novel approach towards robust construction of physical colors on lithium niobate crystal

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Ulrich Kentsch⁴, Shengqiang Zhou⁴, Yuechen Jia^{3,5*}, Feng Chen³ and
Hongliang Liu^{1,6,7*}

Controlling the construction of physical colors on the surfaces of transparent dielectric crystals is crucial for surface coloration and anti-counterfeiting applications. In this study, we present a novel approach to creating stable physical colors on the surface of lithium niobate crystals by combining gold ion implantation with laser direct writing technologies. The interaction between the laser, the implanted gold nanoparticles, and the crystal lattice induces permanent, localized modifications on the crystal surface. By fine-tuning the laser direct writing parameters, we reshaped the gold nanoparticles into spheres of varying sizes on the crystal surface, resulting in the display of red, green, blue, and pale-yellow colors. We investigated the influence of the implanted Au nanoparticles—particularly their localized surface plasmon resonances—on the modifications of the lithium niobate crystal lattice during the laser writing process using confocal Raman spectroscopy and high-resolution transmission electron microscopy. Our findings reveal that the embedded Au nanoparticles play a pivotal role in altering the conventional light-matter interaction between the crystal lattice and the laser, thereby facilitating the generation of surface colors. This work opens new avenues for the development of vibrant surface colors on transparent dielectric crystals.

Keywords: Au ion implantation; laser direct writing; lithium niobate crystal; surface color

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Introduction

Colors profoundly influence the way humans observe, perceive, and understand the world. Throughout the millennia, humans have continually endeavored to reproduce the colors they observe using a variety of methods^{1,2}. Until recent decades, artificial structural col-

ors have become a new focus due to their unique advantages in non-toxicity, sustainability, and durability^{3,4}. Accordingly, they can have multiple functions besides decoration⁵, such as absorbing solar energy^{6,7}, anti-counterfeiting^{8,9}, and information encryption^{10,11}. Up to now, robust physical colors on the surface of metal or glass have

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been achieved through laser direct writing (LDW) by forming complex interactions between the incident light and sophisticated nanostructures^{12–17}. However, these methods heavily depend on the material type and generally, they do not possess the adaptability on other types of materials, especially the pure single crystals with large band gap and anisotropy. In addition, controlling the complex interactions between light and nanostructures is also challenging.

As one of the access to the stable physical color generations, laser induced metal nanoparticles is a plasmonic color generation way due to their subwavelength dimensions^{18,19}. Driven by their diverse chemical and physical properties, as well as their remarkable functionalities in photosensitivity-related applications, gold (Au) nanostructures have garnered significant research attention in recent years^{20–22}. Consequently, a variety of synthetic and nano-processing techniques for Au nanoparticles, towards applications in fields such as nano-photonics, have been developed²³. Ion implantation, a well-established non-equilibrium process, is capable of generating a wide range of metastable solid solutions and has been extensively employed to modify the surface properties of various materials²⁴, including metals²⁵, semiconductors²⁶, and ceramics²⁷. As one of the most promising techniques in nanofabrication, ion implantation has been effectively utilized to synthesize noble metallic nanoparticles embedded within diverse dielectric matrices, such as glasses and crystals^{28,29}. These metallic nanoparticles can behave as the excellent physical base of localized surface plasmon resonance (LSPR) effect. The excitation of LSPR leads to sharp spectral absorption and significant near-field enhancements^{30,31}, in which the resonance wavelength is influenced mostly by the material and morphology of nanostructures³². Notably, intriguing applications, such as optical modulators³³, optical signal processors³⁴, and saturable absorbers³⁵, of LSPR in gold nanoparticles have been reported. However, most research on Au or Ag ion-implanted devices has primarily concentrated on their performance during laser propagation through the materials. Investigations into the interactions between lasers and hybrid ion-implanted materials during laser direct writing on crystal surfaces remain limited³⁶.

LDW is a well-established and versatile technique for fabricating integrated photonic devices^{37,38}. This maskless method offers significant advantages, including flexibility in focusing and the ability to enable cost-effective rapid prototyping, making it competitive with other fab-

rication techniques in terms of manufacturing throughput. Superficial metallic nanoparticles created through ion implantation significantly enhance the optical properties of functional crystals, resulting in an embedded nanoparticle-lattice matter system³⁰. By further combined with LDW, the laser energy is transferred into this hybrid system and significantly enhanced once LDW wavelength matches the LSPR^{39–41}. The integration of these two processes into a single hybrid fabrication procedure enables the formation of larger metallic nanoparticles at the surface, imparting unprecedented functionalities.

In this study, we present a novel approach to creating robust physical colors on lithium niobate (LN) crystals through gold ion implantation and 532 nm laser direct writing. As one of the most widely utilized nonlinear optical crystals, LN exhibits a range of remarkable properties, including exceptional electro-optic, acousto-optic, photorefractive, piezoelectric, and ferroelectric characteristics. Gold ions (Au^+) with an energy of 400 keV are implanted into the crystal surface, resulting in the generation of stable, vivid physical colors through the laser direct writing process. The underlying mechanisms of this phenomena are investigated by employing confocal μ -Raman microscopy, scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). This novel method towards surface color generation in LN crystals paves the way for significant advancements in surface coloring technologies for crystalline materials.

Methods

Sample preparation and metal ion implantation

The LN sample used in this study was commercially acquired from the Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai, China. The raw crystal was cut into a cuboid shape with dimensions of 11 mm (x) $\times$ 10 mm (y) $\times$ 1 mm (z), and both the $x \times y$ facets were optically polished. 400 keV Au^+ -ions at doses of 5×10^{16} ions/cm² were implanted at Helmholtz-Zentrum Dresden-Rossendorf, Germany. And the surface-normal was tilted by 7° with respect to the Au^+ ion beam to avoid the channeling effect. The schematic diagram of Au^+ ion implantation process is illustrated in Fig. 1(a). According to the numerical simulation results calculated by the Stopping and Range of Ions in Matter code (SRIM-2013), the implanted Au^+ -ions are

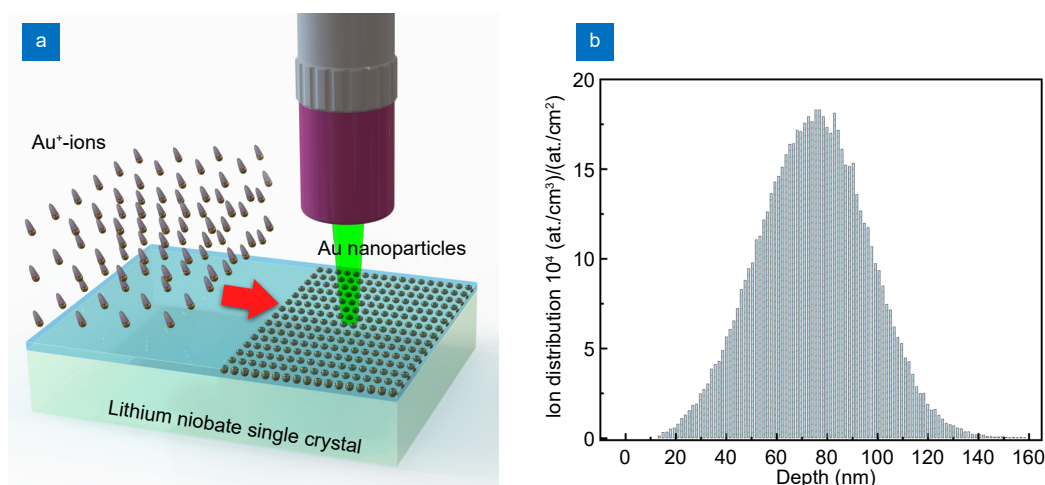


Fig. 1 | (a) Schematic diagrams of ion implantation and laser-induced nanoparticle assembly. (b) The ion distribution of Au⁺-ions calculated by SRIM.

expected to reside approximately 50 to 100 nm beneath the incident sample surface, as shown in Fig. 1(b). As a result, these Au⁺-ions could aggregate and synthesize Au nanoparticles within the bulk sample, as the atomic concentration exceeds the solubility limit.

Laser radiation procedure

During the laser-induced assembly process of nanoparticles, the laser beam generated by a continuous laser at 532 nm (Verdi G-Series, Coherent Inc., USA) propagated through an optical shutter and was then focused onto the ion-implanted sample surface by a long-working-distance microscope objective (50 ×, N.A. = 0.55), as exhibited in Fig. 1(a). A continuous attenuator and several neutral density filters were utilized to control the laser power precisely. The crystal sample was placed on a computer-controlled precise motorized stage (MINI Hybrid Hexapod, ALIO Industries, USA) and the scanning speed was set to 2 mm/s. The actual focusing depth was 5 μm beneath the sample surface. To maintain the dyeing uniformity, the interval of laser scanning lines was set to be 1 μm. The laser radiation process was performed at atmospheric pressure and room temperature.

Characterization of spectrum and nanoparticle morphology

Traditional transmission and reflection microscope spectra were gained by the same Raman spectroscopy system, the spectral signals were intercepted and transmitted to another spectrometer (USB2000+, Ocean Optics, USA).

The morphology characterizations of Au nanoparticles were performed by SEM (FEI Co./ThermoFisher Sci-

entific Inc., USA) and HRTEM (Talos F200X, ThermoFisher Scientific Inc., USA). And these morphology data were used in the subsequent numerical simulations of the optical responses of nanoparticles. For the utilized Finite Difference Time Domain method, the nanoparticles correspond to the classical Lorentz-Drude model. By adjusting the size and density of nanoparticles according to the morphology data, simulated spectra could be obtained.

The influence of ion implantation on lattice structure was characterized by a confocal μ-Raman spectroscopy system (XperRam200, Nanobase, The Republic of Korea). During the Raman property measurement, the 785 nm laser beam with the power of 65 mW was focused onto the implanted surface by a microscope objective (40 ×, N.A. = 0.75). Then, the back-scattered Raman signals were collected and transferred to a spectrum analyzing system with a resolution of 0.8 cm⁻¹. The Galvanometric scanning system can support an in-plane two-dimensional mapping with a spatial resolution up to 100 nm.

Results and discussion

Physical color on sample surface

Due to the high doses of implanted Au⁺-ions, Au nanoparticles can be spontaneously synthesized inside the sample bulk after the ion implantation. Considering the LSPR effect emerges at the boundary of nanoparticle and crystal material, these Au nanoparticles can introduce additional spectrum absorption characteristics. Typical absorption spectrum of LSPR presents one strong absorption peak, and the corresponding wavelength is

related to the morphology of metallic nanoparticles, like the diameters, the interval, and the shapes. Therefore, specific physical color characteristics are endowed to the LN crystal with embedded Au nanoparticles. As a localized effect, LSPR can cause the enhancement of optical field. Therefore, the energy of absorbed spectrum can be transferred to the internal energy under the influence of metal dielectric loss, causing the heating of nanoparticles and surrounding regions. Under higher temperature, the melting of nanoparticles and the "annealing" of surrounding dielectric crystal bulk will lead to the further assembly of Au nanoparticles. Since the physical color characteristics are directly related to the morphology of metallic nanoparticles, the absorption spectrum naturally changes after the assembly of nanoparticles.

Here, four discrete regions were radiated by the 532 nm continuous laser beam with different optical powers respectively. Considering the different morphology pa-

rameters of Au nanoparticles, these regions present different absorption spectra and different physical colors, as shown in Fig. 2. In the following analyses, these regions are represented by their colors as "Region. X", and the labels "Pristine" and "Implanted" represents the raw LN sample and the ion-implanted sample respectively. Obvious color differences appear in the reflection condition, the physical colors at transmission condition are more complex: when the used laser power is relatively low, the transmission and the reflection colors are complementary; as the laser power increases, the transmission and the reflection colors become similar; when the laser power is relatively high, the transmission color turns into white due to the precipitation of nanoparticles and the recovery of crystal lattice. Under this high-energy situation, the modifications on nanoparticles and crystal lattice are saturated, further increment of laser power causes few influences on the present pale-yellow color. The

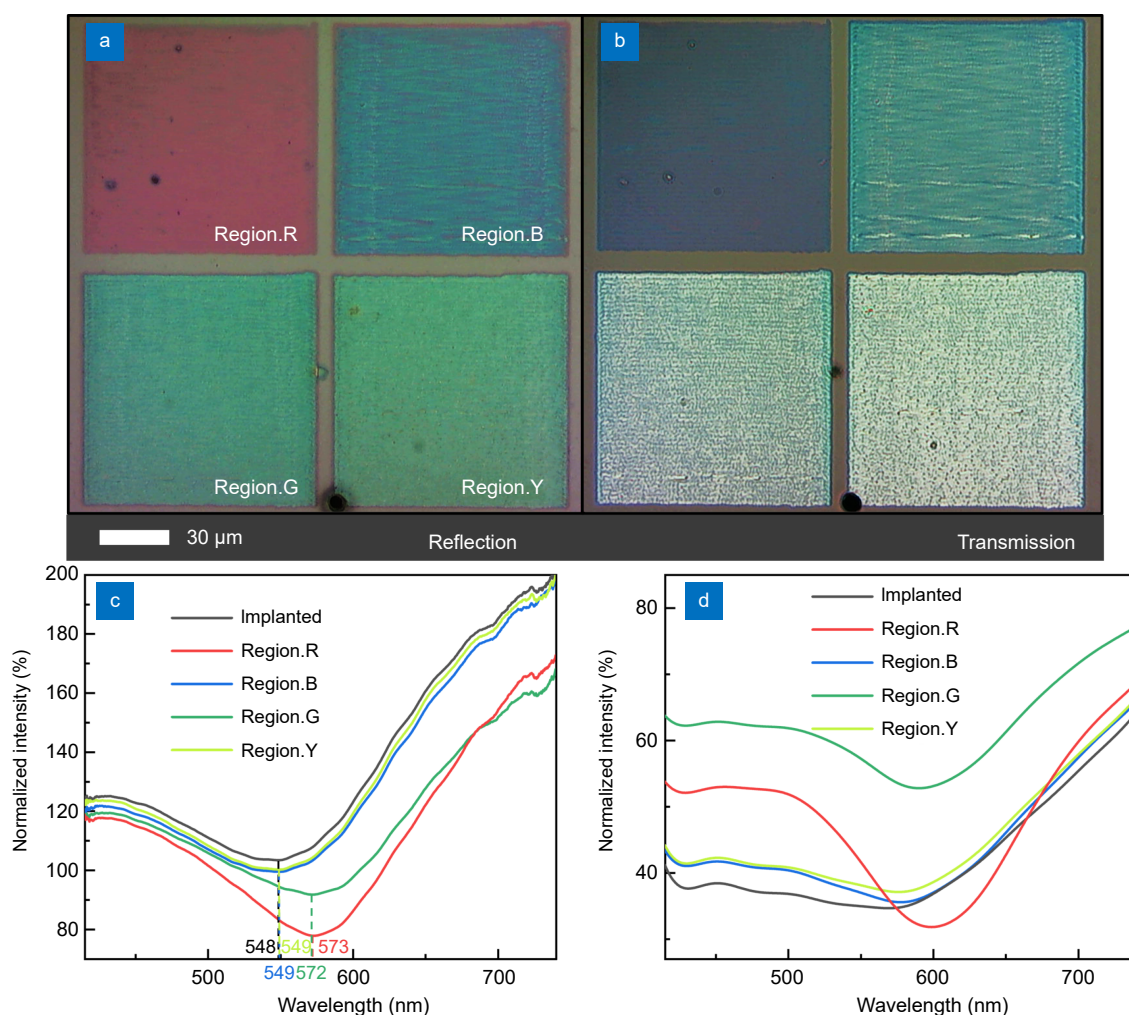


Fig. 2 | The (a) reflection and (b) transmission microscope images of the Au nanoparticles assembly regions with different laser processing energies. (c, d) Corresponding relative microscope spectra. Utilized laser powers for Regions. R, B, G, Y are 17, 29, 53 and 68 mW, respectively.

slight color uniformity is caused by the overlapping of laser scanning trace. Note that the relative microscope spectrum data exhibited here are all normalized according to the corresponding spectrum data of pristine LN crystal sample to eliminate the spectral influence of sample itself, therefore, the spectrum intensity can exceed 100% partially. It should be noticed that, the collective LSPR effect becomes a distribution according to wavelength considering the distributions of diameter and interval of the nanoparticles. In this sense, the actual reflection spectra should be a wide-valley shape instead of the uniform morphology corresponding narrow-linewidth shape. Colors are generated based on such wide-range absorption; thus, the final colors are affected mostly by the spectrum distributions instead of the peak positions (valley in this situation).

The LSPR effect of Au nanoparticles with different morphologies can induce the wide-range absorption in spectrum, resulting in the transmittance reduction in the ion-implanted area. Thus, the laser-unprocessed sample looks darker than the pristine lithium niobate crystal, which can be clearly seen in Fig. 2(b). Due to the spectral distribution of LSPR effect, there will be slight dyeing in this area. However, such dyeing is negligible compared to the colors of laser-processed regions. In this sense, this phenomenon presents no ability to influent the color performance of laser-processed regions.

In this way, specific patterns can be printed onto the ion-implanted sample surface utilizing typical laser direct writing procedure. Here, patterns of letter "NKU" (Nankai University) and the crosshatching with different colors were printed as an example, as exhibited in Fig. 3.

It can be observed in Fig. 3(c) that, when the laser-processed region suffers laser irradiation again, embedded Au nanoparticles will repeat the aggregating and synthesizing process, resulting in the changes in nanoparticle morphologies. Therefore, the final color depends on the nanoparticle morphology, which depends on the laser processing parameters of each experiment. As for the single processing mode, these physical colors present high reproducibility and tolerance on experimental parameters compared to other coloring methods: floating laser powers around the typical value ($\sim \pm 10\%$) for the formation of specific color can induce nearly unanimous colors. From another perspective, such high tolerance limits the color diversity and specific colors of red, blue, green, and pale-yellow with typical HEX val-

ues of 944758, 4d7b90, 4ea07b, and 72b074 can form. However, by integrating the subpixel rendering method, these physical colors (especially the red, blue, and green colors) can work as tricolor, and the attainable color gamut can be significantly expanded.

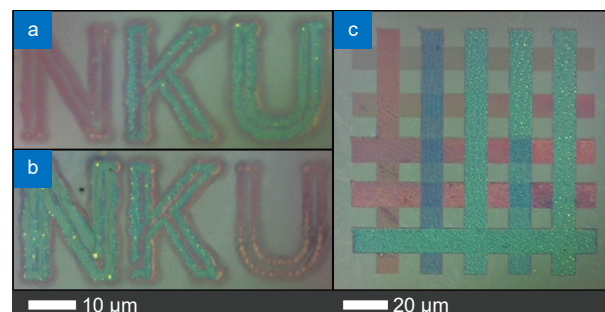


Fig. 3 | The reflection microscope images of (a, b) "NKU" and (c) crosshatching patterned Au nanoparticles assembly regions. Utilized laser powers: (a) patterns "N", "K", "U" are 17, 53 and 68 mW, respectively; (b) patterns "N", "K", "U" are 68, 53 and 17 mW, respectively; (c) horizontal stripes from top to bottom are 6, 12, 15, 19 and 60 mW, respectively; vertical stripes from left to right are 17, 29, 53, 68 and 80 mW.

In addition, these physical colors are formed based on the LSPR effect of embedded Au nanoparticles, which are well-protected by the lithium niobate crystal lattice structure. Therefore, the colors are very stable. The sample has been immersed in anhydrous ethanol for ultrasonic bath, wiped forcefully by cotton swab, and stored at room temperature for more than 6 months, there are still no variations on these colors.

Nanoparticle morphology and LSPR spectroscopy

Considering the decisive influence of Au nanoparticle morphology on physical color, performing direct observation of nanoparticles should be a necessary option. Therefore, top-view SEM and side-face HRTEM measurements on the laser-processed surface were realized respectively, as shown in Fig. 4. As the laser processing energy increases, larger Au nanoparticles will form and precipitate through the ion-implanted sample surface, remaining amorphous Au element and nanoparticles with smaller size. The evolution rules of these remained Au nanoparticles under different laser processing energies are quite complex, and typical morphology parameters of these nanoparticles in different laser-processed regions are listed in Table 1. During the formation of Au nanoparticles, the Au⁺-ions implanted lithium niobate materials are in the status of amorphous,

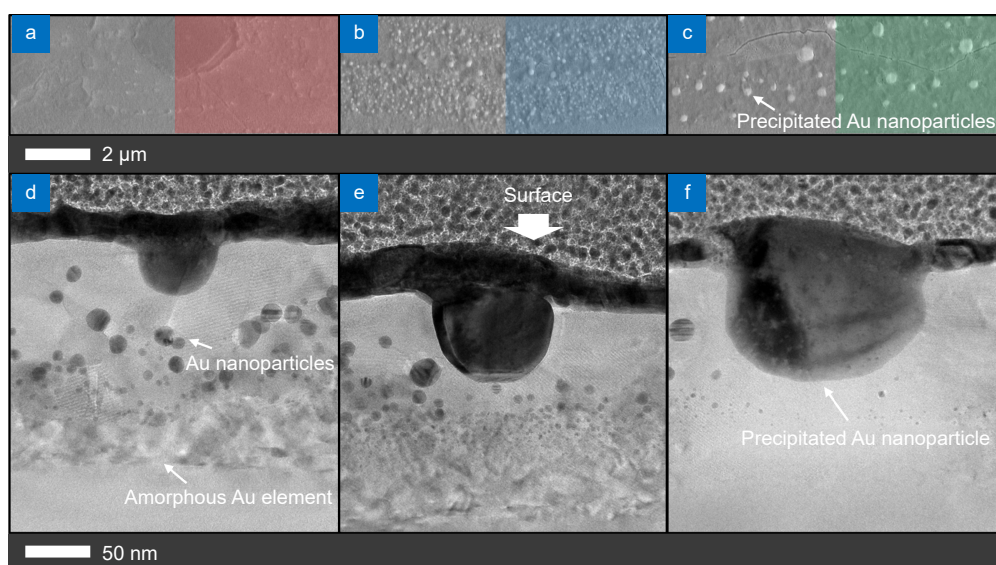


Fig. 4 | (a–c) Surface SEM images and (d, e) corresponding cross-sectional HRTEM images of the Au nanoparticles assembly regions. Utilized laser powers: (a, d) 17 mW; (b, e) 29 mW; (c, f) 53 mW, respectively.

Table 1 | Laser powers, reflection colors, resonance wavelengths and typical nanoparticle morphology parameters of the bulk material, ion-implanted surface and laser-processed regions.

Region	Laser power (mW)	Color (reflection)	Resonance wavelength (reflection)	Typical diameter of nanoparticles (nm)	Typical interval of nanoparticles (nm)
Pristine	0	/	/	/	/
Implanted	0	/	548.37	1.7	25
Region. R	17	Red	573.25	3.7	17
Region. B	29	Blue	549.44	2.3	25
Region. G	53	Green	572.19	2.5	20
Region. Y	68	Pale-yellow	548.95	2	25

then nanocrystalline, and monocrystal as there no Au^{+} ions exist in the sedimentary area. It should be noted that the white spots in SEM images and the largest-size spheres are all precipitated Au nanoparticles, and since their morphology parameters do not meet LSPR requirements, these nanoparticles make no contribution to the physical color. Instead, the remaining smaller Au nanoparticles dominate the LSPR effect and decide the physical color. Detailed colors, experimental laser powers, and corresponding nanoparticle morphology parameters are listed in Table 1.

Using the Au nanoparticle morphology parameters generalized from Fig. 4, LSPR effect and corresponding resonance peak (valley in this situation) could be numerically calculated and illustrated as the relative reflection spectra in Fig. 5(a). Simultaneously, the relative electric field intensity distribution of LSPR example is shown in Fig. 5(b). The nanoparticle morphology parameters listed in Table 1 are gained according to the distribution

mode of HRTEM data. The resonance wavelengths of corresponding numerical calculations are in accordance with the experimental results. However, considering the morphology distribution of Au nanoparticles, the actual reflection spectra should be a collective LSPR effect of these nanoparticles. Such spectrum should be the combination of these LSPR spectra instead of single numerical calculation result under specific nanoparticle morphology parameter. An example is given by a simple linear mathematical operation of these numerical relative reflection spectra, in which the spectral line profile is similar to the experimental reflection spectra in Fig. 2.

Lattice dynamics

Particular lattice structure corresponds to specific Raman spectrum, thus the lattice dynamics can be revealed by the differences of Raman phonon modes⁴². Under R3c space group, the Raman phonon modes of LN at room temperature can be described by the irreducible

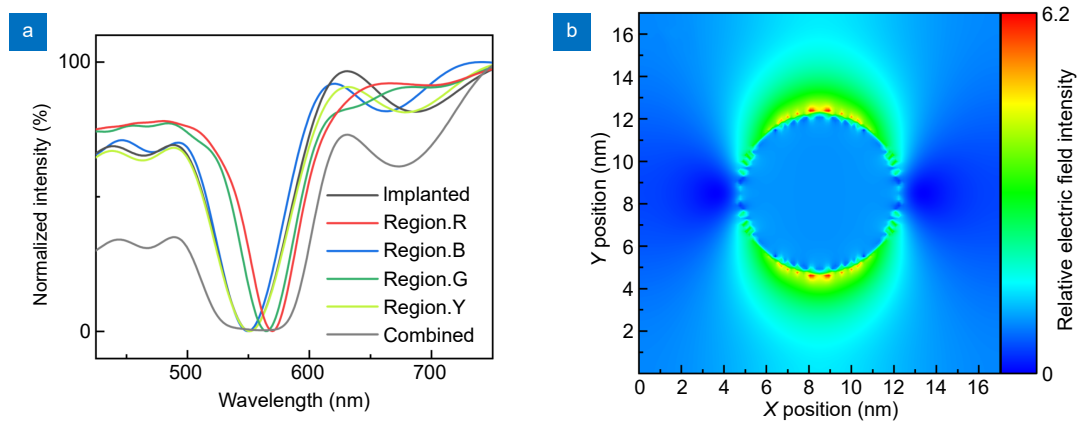


Fig. 5 | (a) Numerical calculations of the relative reflection spectra using the nanoparticle morphology parameters in Table 1. (b) The electric field intensity distribution under LSPR situation (resonance wavelength 573 nm, nanoparticle diameter 3.7 nm, nanoparticle interval 17 nm).

representations $5A_1 + 5A_2 + 10E$, as the Group Theory predicts. The absolute-intensity Raman spectra of raw material, ion-implanted sample, and the laser-processed regions are illustrated in Fig. 6(a), corresponding phonon symmetries and branches are marked around the Raman peak. Obvious intensity differences can demonstrate the changes of lattice deformation and damage: raw material presents largest spectrum intensity; strong quenching after the ion implantation has happened because of the strong lattice damage caused by the

ion-bulk interaction and the formation of Au nanoparticles; and after the laser radiation, such lattice damage will partially recovery since the Au nanoparticles can further aggregate, resulting in the spectrum intensity recovery at the same time. Similarly, samples with higher lattice damage generally present higher baseline intensity, therefore, corresponding relative intensities of the phonon modes are lower simultaneously. In this sense, different absolute spectrum intensities with different laser radiation powers can be ascribed to the different

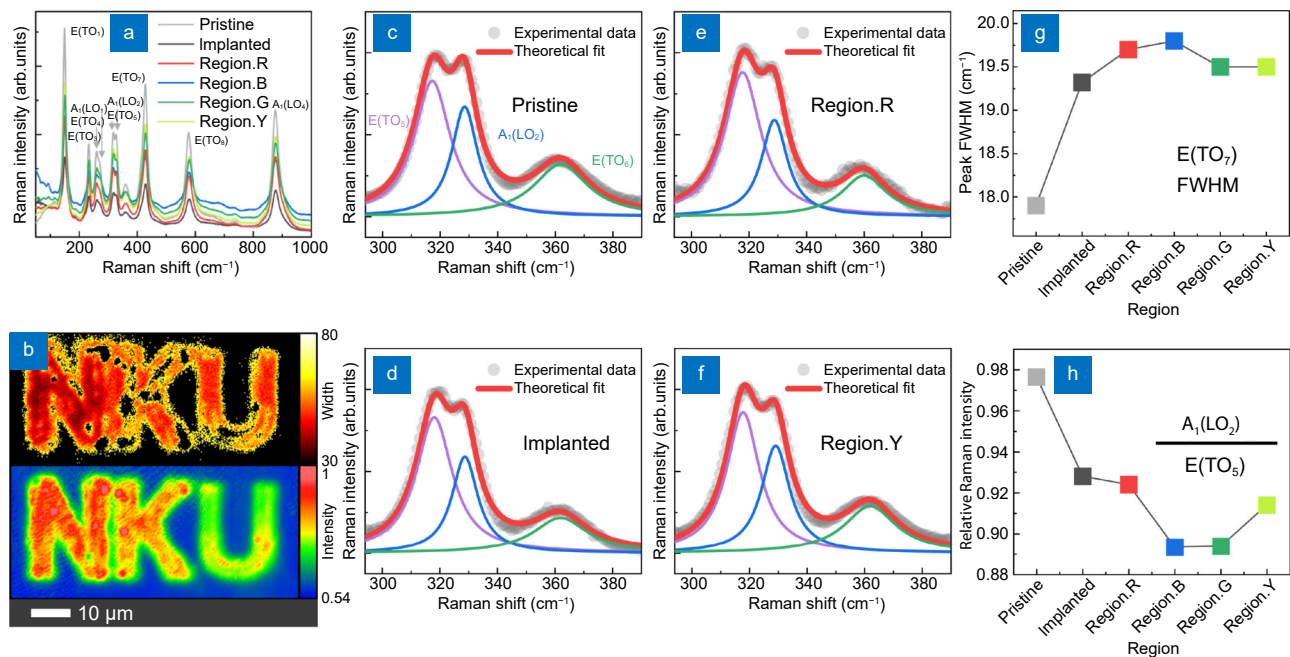


Fig. 6 | Raman spectroscopy analysis. (a) Raman spectra of the bulk material, ion-implanted surface and laser-processed regions. (b) Two-dimensional Raman mapping images of the pattern in Fig. 3(b) with the imaging channels of $E(TO_7)$ peak FWHM and intensity. Utilized laser powers for patterns “N”, “K”, “U” are 68, 53 and 17 mW, respectively. (c–f) $E(TO_5)$ - $A_1(LO_2)$ double-peak Raman fitting curves of the bulk material, ion-implanted surface and laser-processed regions. Utilized laser powers for Regions. B and Y are 29 and 68 mW, respectively. (g) $E(TO_7)$ peak FWHM and (h) $E(TO_5)$ - $A_1(LO_2)$ double-peak relative intensity differences of the bulk material, ion-implanted surface and laser-processed regions.

aggregating progresses of Au nanoparticles. Two-dimensional Raman property mapping results of the inferior "NKU" pattern shown in Fig. 3(b) indicate similar conclusions on intensity change. The peak width (defined as the full width at half maximum, FWHM) channel image also suggests the recovery of lattice damage after laser radiation, as exhibited in Fig. 6(b).

Since typical Raman phonon mode corresponds to specific lattice vibration mode, the changes on peak intensity and FWHM can be used to determine the lattice deformation and damage quantitatively. However, overlapping of adjacent Raman peaks will severely affect the analyses of Raman phonon mode differences, especially for the double-peak situation. Therefore, in the sense of spectroscopy, using numerical models to fit the raw spectrum data provides higher accuracy⁴³. Here, the damped harmonic oscillator model is sufficient for the description of simple phonon peaks:

$$I(\omega) = \sum_i \frac{A_i \Gamma_i \omega_i^2}{(\omega^2 - \omega_i^2)^2 + \omega^2 \Gamma_i^2},$$

where A_i , ω_i , and Γ_i are the intensity, the frequency, and the damping constant of the i th Raman mode, respectively. Typical Raman modes were selected and fitted for further analysis: the E(TO₅) and A₁(LO₂) double-peak at ~320 cm⁻¹, the highest single E(TO₇) peak at 426 cm⁻¹, and the fitting diagrams of E(TO₅)-A₁(LO₂) double-peak under different laser-processed regions are illustrated in Fig. 6(c-f).

Then, detailed Raman spectroscopy analyses based on the spectrum data of E(TO₇) single peak and E(TO₅)-A₁(LO₂) double-peak have been analyzed. Corresponding FWHM or relative intensity data are collected and illustrated in Fig. 6(g, h). Considering wider FWHM represents more intense lattice damage, the FWHM changes of the E(TO₇) peak exhibited in Fig. 6(g) indicate such conclusion: before the ion implantation process, the LN sample keeps pure lattice structure without any obvious lattice damage or deformation; the ion-matter interaction during the ion implantation and the formed metallic nanoparticles can introduce lattice damage and deformation into the pure lattice structure; after laser processing with relatively low energy, the assembly of Au nanoparticles can cause the change of nanoparticle morphology, resulting in the formation of new Au nanoparticles with larger size. Such embedded large metallic nanoparticles can induce relatively strong lattice damage. As the used laser energy increases, larger Au nanoparti-

cles can form inside the LN sample. At the same time, more intensive extrusion effect from the surrounding lattice structure can cause the directional movement of large nanoparticles toward the sample surface. Finally, the precipitation of large Au nanoparticles will happen, remaining small nanoparticles and amorphous Au element.

The relative intensity differences of E(TO₅)-A₁(LO₂) double-peak on different laser-processed regions shown in Fig. 6(h) demonstrate similar results. Compared to the transverse optical phonon mode, longitudinal optical phonon mode is more susceptible to the influence of long-range order, thus, lattice deformation can cause more severe activity reduction. The relative intensity changes of E(TO₅)-A₁(LO₂) (defined as intensity ratio A₁(LO₂)/E(TO₅)) under different laser processing energies present similar trends, which indicates that the physical mechanisms of lattice deformation and lattice damage are homologous. It should be noticed that such changes on peak intensity and FWHM occurs at almost all Raman phonon modes, which suggests the lattice deformation and damage induced by the embedded metallic nanoparticles are relatively uniform.

Conclusions

In summary, we have demonstrated a novel method for generating stable and vivid physical colors on the surface of LN crystals using the combination of metallic ion implantation and LDW technologies. Through the interaction of the laser with Au nanoparticles and the crystal lattice, permanent and localized modifications are introduced into the crystal surface. Simultaneous morphology changes of Au nanoparticles can cause the shift of LSPR peak, resulting in the different physical colors: red, green, blue, and pale-yellow by adjusting the LDW parameters. Confocal Raman spectroscopy, SEM and HRTEM analyses reveal that the embedded Au nanoparticles altered the light-matter interaction system between the crystal lattices and the lasers, contributing to the generation of surface colors. This study reveals new possibilities for developing vibrant surface colors on crystalline materials, with potential applications in surface coloring and anti-counterfeiting technologies.

References

1. Liu K, Lin ZY, Han B et al. Non-volatile dynamically switchable color display via chalcogenide stepwise cavity resonators. *Opto-Electron Adv* 7, 230033 (2024).

2. Jia JY, Ban Y, Liu K et al. Reconfigurable full color display using anisotropic black phosphorus. *Adv Opt Mater* 9, 2100499 (2021).
3. Cao T, Zhang XY, Dong W et al. Tuneable thermal emission using chalcogenide metasurface. *Adv Opt Mater* 6, 1800169 (2018).
4. Ban Y, Jia JY, Zhan Y et al. A black phosphorus-based Fabry–Pérot cavity and its application for reversible color switching. *Adv Photonics Res* 3, 2200137 (2022).
5. Lu TW, Lin Y, Zhang TQ et al. Self-polarized RGB device realized by semipolar micro-LEDs and perovskite-in-polymer films for backlight applications. *Opto-Electron Adv* 7, 230210 (2024).
6. Li ZP, Li SN, Ma T. Using photonic glasses as colored covers for solar energy harvesting. *Adv Opt Mater* 11, 2202370 (2023).
7. Soman A, Antony A. Colored solar cells with spectrally selective photonic crystal reflectors for application in building integrated photovoltaics. *Sol Energy* 181, 1–8 (2019).
8. Li A, Yang DP, Cao C et al. Mechano-chromic photonic crystals with substrate-independent brilliant colors for visual sensing and anti-counterfeiting applications. *Adv Mater Interfaces* 9, 2200051 (2022).
9. Sun Y, Le XX, Zhou SY et al. Recent progress in smart polymeric gel-based information storage for anti-counterfeiting. *Adv Mater* 34, 2201262 (2022).
10. Li HT, Zhu MJ, Tian F et al. Polychrome photonic crystal stickers with thermochromic switchable colors for anti-counterfeiting and information encryption. *Chem Eng J* 426, 130683 (2021).
11. Dong SN, Zheng QQ, Tang MQ et al. Ionic microgel colloidal crystals: responsive chromism in dual physical and chemical colors for high-end information security and encryption. *ACS Appl Mater Interfaces* 15, 33985–33997 (2023).
12. Sun K, Tan DZ, Fang XY et al. Three-dimensional direct lithography of stable perovskite nanocrystals in glass. *Science* 375, 307–310 (2022).
13. Geng J, Xu LY, Yan W et al. High-speed laser writing of structural colors for full-color inkless printing. *Nat Commun* 14, 565 (2023).
14. Roberts AS, Novikov SM, Yang YQ et al. Laser writing of bright colors on near-percolation plasmonic reflector arrays. *ACS Nano* 13, 71–77 (2019).
15. Fraggelakis F, Tsididis GD, Stratakis E. Ultrashort pulsed laser induced complex surface structures generated by tailoring the melt hydrodynamics. *Opto-Electron Adv* 5, 210052 (2022).
16. Zhang YC, Jiang QL, Long MQ et al. Femtosecond laser-induced periodic structures: mechanisms, techniques, and applications. *Opto-Electron Sci* 1, 220005 (2022).
17. Jiang QL, Chen L, Liu JK et al. Periodic transparent nanowires in ITO film fabricated via femtosecond laser direct writing. *Opto-Electron Sci* 2, 220002 (2023).
18. Guay JM, Calà Lesina A, Côté G et al. Laser-induced plasmonic colours on metals. *Nat Commun* 8, 16095 (2017).
19. Liu ZM, Vitrant G, Lefkir Y et al. Laser induced mechanisms controlling the size distribution of metallic nanoparticles. *Phys Chem Chem Phys* 18, 24600–24609 (2016).
20. Zare I, Yarak MT, Speranza G et al. Gold nanostructures: synthesis, properties, and neurological applications. *Chem Soc Rev* 51, 2601–2680 (2022).
21. Kim HJ, Hossen MM, Hillier AC et al. Interfacial and bulk assembly of anisotropic gold nanostructures: Implications for photonics and plasmonics. *ACS Appl Nano Mater* 3, 8216–8223 (2020).
22. Zhou WJ, Shi JZ, Chen RY et al. Aggregation of gold nanoparticles for controlling emission polarization: Implications for applications in photonics. *ACS Appl Nano Mater* 7, 15025–15034 (2024).
23. Guglielmelli A, Pierini F, Tabiryan N et al. Thermoplasmonics with gold nanoparticles: a new weapon in modern optics and biomedicine. *Adv Photonics Res* 2, 2000198 (2021).
24. Yang QX, Li XJ, Liu HL et al. Obvious phase transition status induced by He⁺-ions implantation in KTN crystal. *Acta Mater* 221, 117376 (2021).
25. Wei X, Liu PD, Ma SJ et al. Improvement on corrosion resistance and biocompatibility of ZK60 magnesium alloy by carboxyl ion implantation. *Corros Sci* 173, 108729 (2020).
26. Das A, Basak D. Efficacy of ion implantation in zinc oxide for optoelectronic applications: a review. *ACS Appl Electron Mater* 3, 3693–3714 (2021).
27. Athanasiou CE, Zhang HL, Ramirez C et al. High toughness carbon-nanotube-reinforced ceramics via ion-beam engineering of interfaces. *Carbon* 163, 169–177 (2020).
28. Devarani Devi K, Sharma A, Ojha S et al. Effect of isothermal annealing on the bimetallic gold-silver nanoparticles synthesized by sequential implantation in quartz matrices and their surface Plasmon resonance properties. *Mater Today Commun* 40, 109488 (2024).
29. Yamada T, Fukuda K, Semboshi S et al. Control of optical absorption of silica glass by Ag ion implantation and subsequent heavy ion irradiation. *Nanotechnology* 31, 455706 (2020).
30. Wu B, Zhu H, Zhang B et al. Plasmon guided assembly of nanoparticles in solids. *Mater Today Nano* 21, 100299 (2023).
31. Zhu H, Chu LR, Liu WJ et al. Ultrafast laser - induced plasmonic modulation of optical properties of dielectrics at high resolution. *Adv Opt Mater* 11, 2300929 (2023).
32. Dahan KA, Li Y, Xu J et al. Recent progress of gold nanostructures and their applications. *Phys Chem Chem Phys* 25, 18545–18576 (2023).
33. Ionut Bercea A, Champeaux C, Boule A et al. Adaptive gold/vanadium dioxide periodic arrays for infrared optical modulation. *Appl Surf Sci* 585, 152592 (2022).
34. Chauhan M, Kumar Singh V. Review on recent experimental SPR/LSPR based fiber optic analyte sensors. *Opt Fiber Technol* 64, 102580 (2021).
35. Chu LR, Zhu H, Sun XL et al. Gold-nanoparticles induced transition in YVO₄ crystal: from saturable to reverse saturable absorption. *Opt Mater* 135, 113342 (2023).
36. Li SS, Fang YN, Wang JF. Control of light-matter interactions in two-dimensional materials with nanoparticle-on-mirror structures. *Opto-Electron Sci* 3, 240011 (2024).
37. Tan DZ, Zhang B, Qiu JR. Ultrafast laser direct writing in glass: Thermal accumulation engineering and applications. *Laser Photonics Rev* 15, 2000455 (2021).
38. Lai SQ, Liu SB, Li ZL et al. Applications of lasers: a promising route toward low-cost fabrication of high-efficiency full-color micro-LED displays. *Opto-Electron Sci* 2, 230028 (2023).
39. Berhe AM, As'ham K, Al-Ani I et al. Strong coupling and catenary field enhancement in the hybrid plasmonic metamaterial cavity and TMDC monolayers. *Opto-Electron Adv* 7, 230181 (2024).
40. Chen LW, Hong MH. Functional nonlinear optical nanoparticles synthesized by laser ablation. *Opto-Electron Sci* 1, 210007 (2020).

(2022).

41. Chen LW, Jiang XF, Guo ZM et al. Tuning optical nonlinearity of laser-ablation-synthesized silicon nanoparticles via doping concentration. *J Nanomater* **2014**, 652829 (2014).
42. Fontana MD, Bourson P. Microstructure and defects probed by Raman spectroscopy in lithium niobate crystals and devices. *Appl Phys Rev* **2**, 040602 (2015).
43. Zanatta AR. Raman spectroscopy of lithium niobate (LiNbO₃) – sample temperature and laser spot size effects. *Results Phys* **47**, 106380 (2023).

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Author contributions

Yuechen Jia and Hongliang Liu proposed the original idea and supervised the project. Quanxin Yang, Menghan Yu, and Zhixiang Chen performed the main experiments and measurements. Siwen Ai helped the LDW process. Ulrich Kentsch and Shengqiang Zhou performed the metal ion implantation. Feng Chen provided constructive suggestions and feedback. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing financial interests.



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