

Supplementary Information for

Defocused Laser-Induced Self-Powered Microneedle Patches for

Drug-Releasing and Wound Monitoring

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Note S1. Laser gaussian beam propagation and spot control

The CO₂ laser beam propagates as a Gaussian beam, characterized by its intensity distribution and beam divergence. The spot radius of a Gaussian beam at axial position z from the beam waist is given by:

$$w(z) = w_0 \sqrt{1 + (z/z_R)^2}$$

where $w(z)$ is the beam radius at position z , w_0 is the minimum spot radius at the focal point (beam waist), and z_R is the Rayleigh length defined as:

$$z_R = \pi w_0^2 / \lambda$$

where λ is the laser wavelength. The Rayleigh length represents the distance over which the beam remains relatively focused.

The intensity distribution of a Gaussian beam exhibits both radial and axial variations. At any axial position z , the intensity at radial distance r from the beam axis follows:

$$I(r, z) = I_0(z) e^{-2r^2/w^2(z)}$$

where $I_0(z)$ is the peak intensity on the beam axis. This peak intensity is related to the total laser power P by:

$$I_0(z) = 2P / [\pi w^2(z)]$$

This relationship demonstrates that peak intensity is inversely proportional to the square of the spot radius. At the focal point where $w(z)=w_0$ is minimum, the intensity reaches its maximum value.

Under different focal conditions, the beam geometry at the material surface varies significantly. For positive defocus, where the focal point is positioned above the material surface by distance Δz , the spot radius at the material surface is:

$$w_s = w_0 \sqrt{1 + (\Delta z/z_R)^2}$$

For negative defocus, where the focal point is buried beneath the material surface at depth Δz , and considering material depth d , the spot radius at depth d is:

$$w_n = w_0 \sqrt{1 + (|d - \Delta z|/z_R)^2}$$

These equations quantitatively describe how beam divergence affects spot size at different focal positions, directly influencing ablation geometry.

41 **Note S2. Energy density and thermal effects**

42 The laser fluence (energy density per pulse) determines whether ablation occurs. For a single laser pulse
43 with energy E , the fluence at the beam center is:

$$F_0 = 2E/(\pi w^2)$$

44 where F_0 is expressed in J/cm². This demonstrates that fluence scales inversely with the square of the
45 spot radius.

46 Material removal occurs only when local laser intensity exceeds the material-specific ablation
47 threshold F_{th} . The threshold criterion is:

$$I(r, z) \geq I_{th}$$

48 Equivalently, for pulsed lasers, the threshold can be expressed in terms of fluence: $F_0 \geq F_{th}$, where F_{th}
49 is the threshold fluence.

50 For materials with absorption coefficient α , the ablation depth per pulse can be approximated by:

$$d_\alpha = \left(\frac{1}{\alpha}\right) \ln (F_0/F_{th})$$

51 This logarithmic relationship indicates that ablation depth increases with fluence, but with
52 diminishing returns at higher fluence values. The absorption coefficient α represents the inverse of the
53 optical penetration depth.

54 The ablated diameter at depth z depends on the spatial intensity distribution. Solving the threshold
55 condition yields the ablation radius:

$$r_\alpha(z) = w(z) \sqrt{[\ln (\frac{F_0(z)}{F_{th}})]/2}$$

56 This expression shows how the ablated diameter varies with depth, leading to the characteristic
57 conical geometry observed in laser drilling.

58 The temperature evolution in the material during laser irradiation is governed by the
59 three-dimensional heat conduction equation:

$$\rho C_p \left(\frac{\partial T}{\partial t}\right) = \nabla \cdot (k \nabla T) + Q_{laser}$$

60 where ρ is material density, C_p is specific heat capacity, T is temperature, k is thermal conductivity,
61 and Q_{laser} is the volumetric heat source term from laser absorption.

The volumetric heat generation due to laser absorption follows the Beer-Lambert law:

$$Q_{\text{laser}}(r, z, t) = \alpha I(r, 0, t) e^{-\alpha z}$$

where α is the absorption coefficient, $I(r, 0, t)$ is the laser intensity distribution, and the exponential term accounts for intensity attenuation with depth.

For a Gaussian heat source, the peak temperature rise at the beam center can be approximated by:

$$\Delta T \approx \alpha F_0 / \rho C_p$$

This simplified expression shows that temperature rise is directly proportional to fluence and absorption coefficient, while inversely proportional to the volumetric heat capacity ρC_p . The morphological trends observed in Fig. 2 are consistent with this theoretical analysis.

Note S3. Plasma Formation and Shielding Effects

Plasma formation occurs when laser intensity is sufficient to ionize the ablated material vapor or surrounding air. The plasma formation threshold scales inversely with both wavelength squared and pulse duration:

$$I_{\text{th,bd}} \propto 1/\lambda^2 \tau_p$$

where λ is wavelength, τ_p is pulse duration. CO₂ lasers (10.6 μm) reach the breakdown threshold at relatively modest intensities, making plasma effects significant in CO₂ laser micromachining.

The critical electron density at which plasma becomes opaque to laser radiation is:

$$n_c = \varepsilon_0 m_e \omega_L^2 / e^2$$

where ε_0 is vacuum permittivity, ω_L is laser angular frequency ($\omega_L = 2\pi c/\lambda$), and e is elementary charge. For CO₂ lasers ($\lambda = 10.6 \mu\text{m}$), $n_c \approx 10^{19} \text{ cm}^{-3}$

Once formed, plasma absorbs and scatters incoming laser radiation, reducing effective intensity reaching the material surface. The transmitted intensity through a plasma layer of length L is:

$$I_{\text{trans}} = I_0 e^{-\alpha_{\text{plasma}} L}$$

where α_{plasma} is the plasma absorption coefficient. The fraction of laser energy absorbed by plasma is:

$$A_{\text{plasma}} = 1 - \exp(-\alpha_{\text{plasma}} L)$$

Under positive defocus conditions, air plasma forms between the focal point and material surface, significantly reducing ablation efficiency. Under negative defocus, plasma formation occurs closer to or within the developing microhole. Rather than attenuating the beam before it reaches the surface, this localized plasma may modify local energy coupling and assist material removal within the cavity, which is consistent with the observed deeper and sharper microholes.

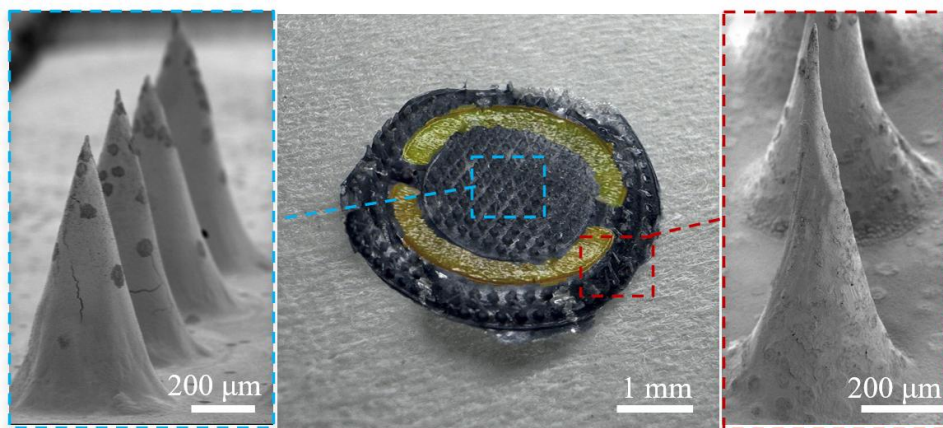
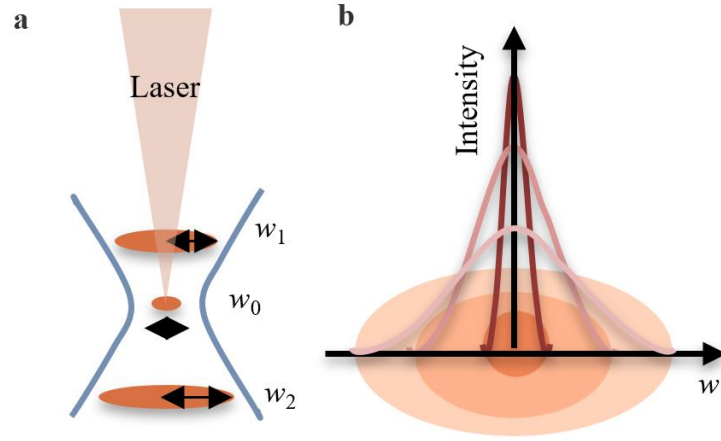


Fig. S2 Surface morphologies of the SPMNP with SEM images of microneedles from central and edge regions. Colorimetric sensing areas are integrated around the microneedle array. Left image: central region microneedles with uniform spacing and relatively thick structure. Right image: edge region microneedles demonstrating sharp morphology.



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98 **Fig. S3** Intrinsic characteristics of CO₂ laser beam propagation and intensity distribution. **a** Gaussian
 99 beam propagation showing convergence to minimum beam waist w_0 at the focal point. **b** Gaussian
 100 intensity distribution profile with the highest intensity at beam center.

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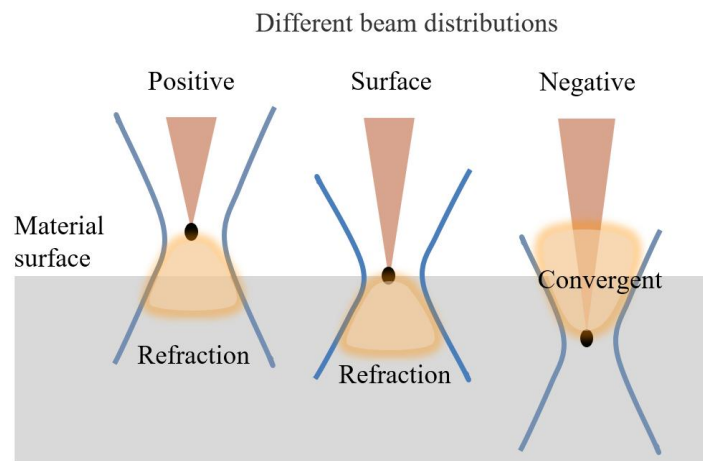


Fig. S4 The relative position of the focus with respect to the workpiece.

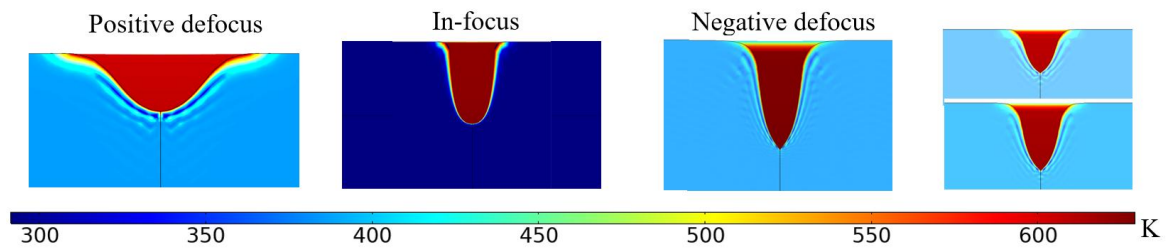


Fig. S5 Simulations of laser ablation results under different focal distances, demonstrating shallow ablation with positive defocus, moderate penetration with in-focus conditions, and deepest penetration with sharpest geometry under negative defocus.

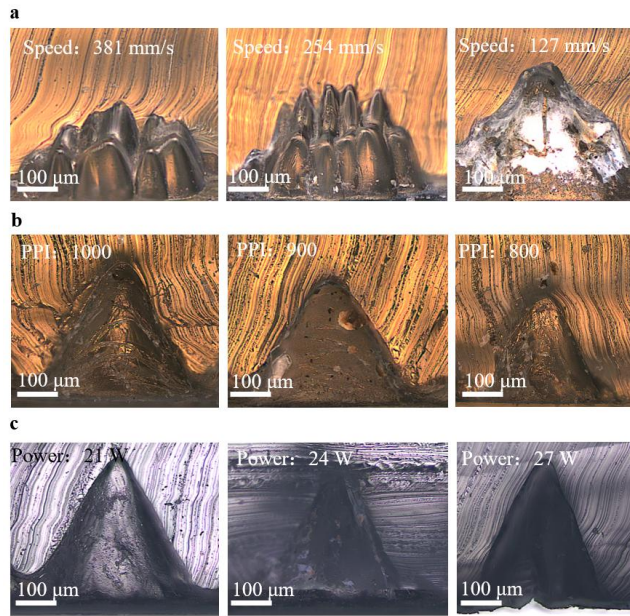


Fig. S6 Effects of laser processing parameters on microneedle mold morphology and geometry. **a** Influence of laser speed (381, 254, 127 mm/s) variations on ablated micro-hole characteristics (PPI: 900, power: 24 W). **b** Effect of PPI (1000, 900, 800) variations on ablation depth and profile geometry (speed: 127 mm/s, power: 24 W). **c** Laser power effects (21 W, 24 W, 27 W) on ablation characteristics (PPI: 900, speed: 127 mm/s).

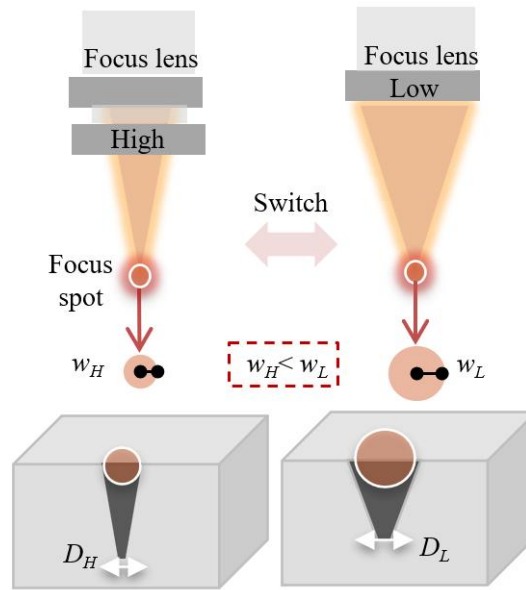


Fig. S7 Comparison of high-magnification and low-magnification focusing lens effects on laser processing characteristics.

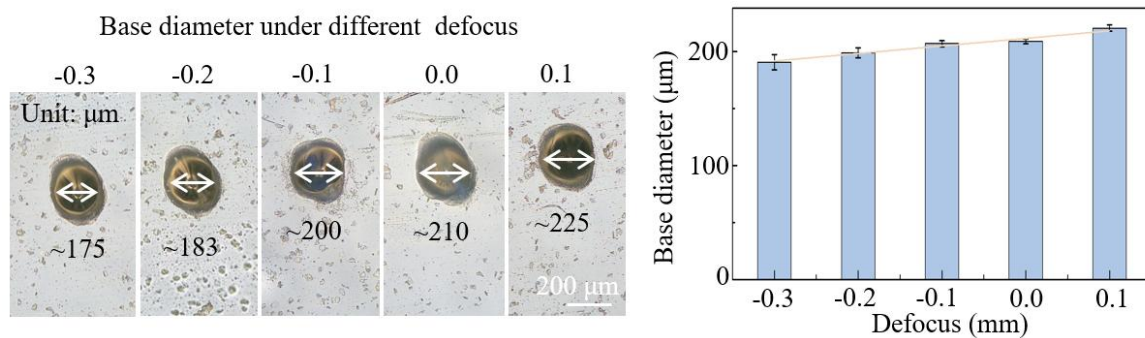
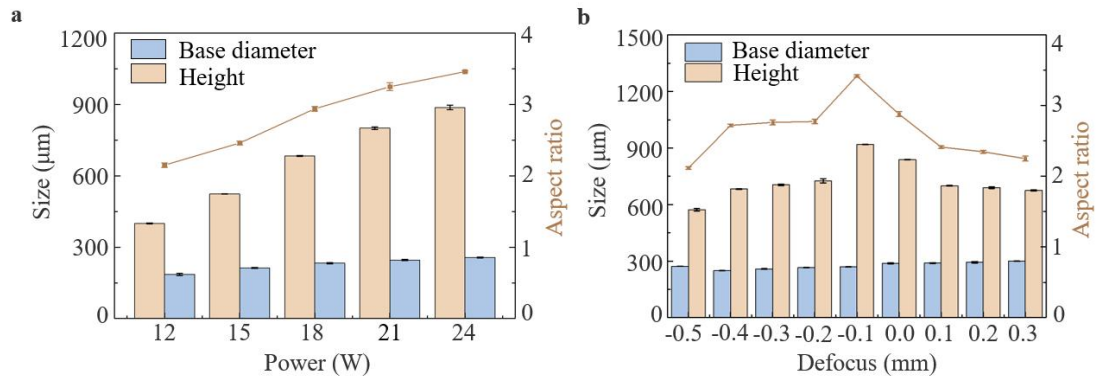


Fig. S8 Effect of defocus distance on diameters of microneedle bases. Optical microscopy images and quantitative analysis showing gradual increase in base diameter from $\sim 175 \mu\text{m}$ at -0.3 mm defocus to $\sim 225 \mu\text{m}$ at $+0.1 \text{ mm}$ defocus (PPI: 900, power: 24 W). Data were presented as means $\pm$ SD, $n = 3$.



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Fig. S9 Effects of laser power and defocus distance on microneedle dimensional characteristics. **a** Microneedle morphological variations with increasing laser power from 12 W to 24 W (defocus: -0.1 mm, PPI: 900). **b** Effects of defocus distance on microneedle dimensions across -0.5 mm to +0.3 mm range (power: 24 W, PPI: 900). Data in (a) and (b) were presented as means $\pm$ SD, $n = 3$.

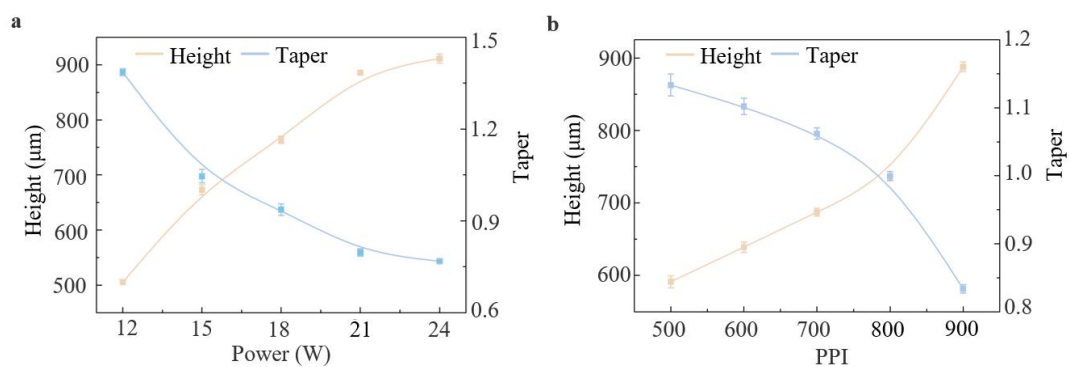


Fig. S10 Effects of **a** laser power and **b** PPI on microneedle height and taper under low-magnification focusing lens. Data in **a** and **b** were presented as means $\pm$ SD, $n = 3$.

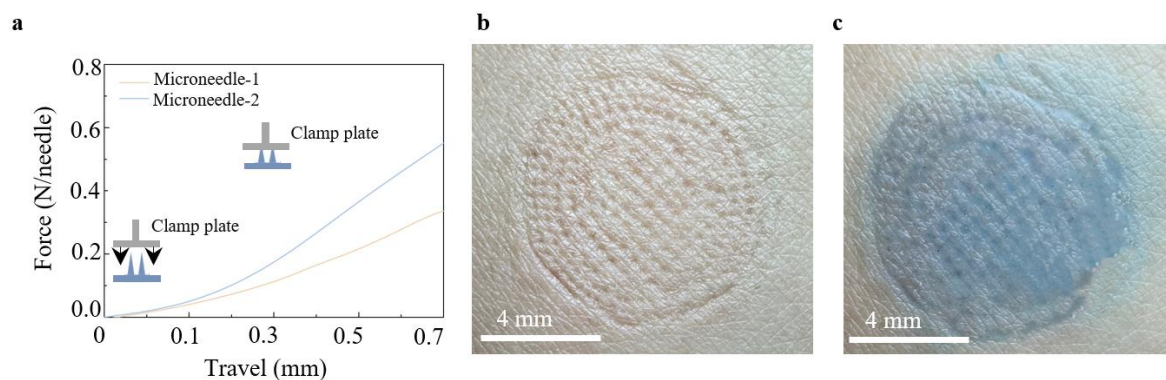


Fig. S11 **a** Mechanical strength testing of microneedles with different tip sizes. Microneedle-1 and microneedle-2 represent microneedles fabricated using high-magnification focusing lens and low-magnification focusing lens, respectively. **b**, **c** Skin marks and staining effects following patch removal.

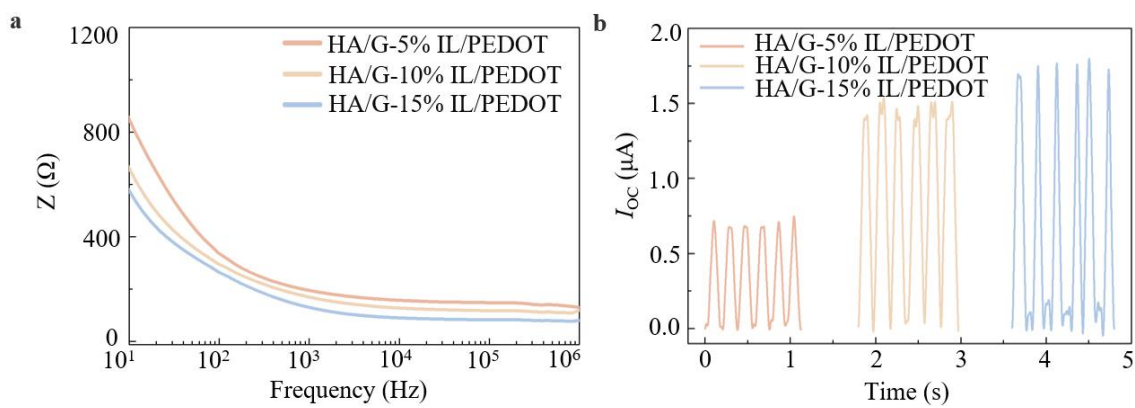


Fig. S12 Electrical properties of the ES-MNP. **a** EIS measurement of the HA/G-IL/PEDOT:PSS films with an Ag/AgCl RE and a Pt CE. **b** Short-circuit current output of the ES-MNP with different IL/PEDOT:PSS concentrations.

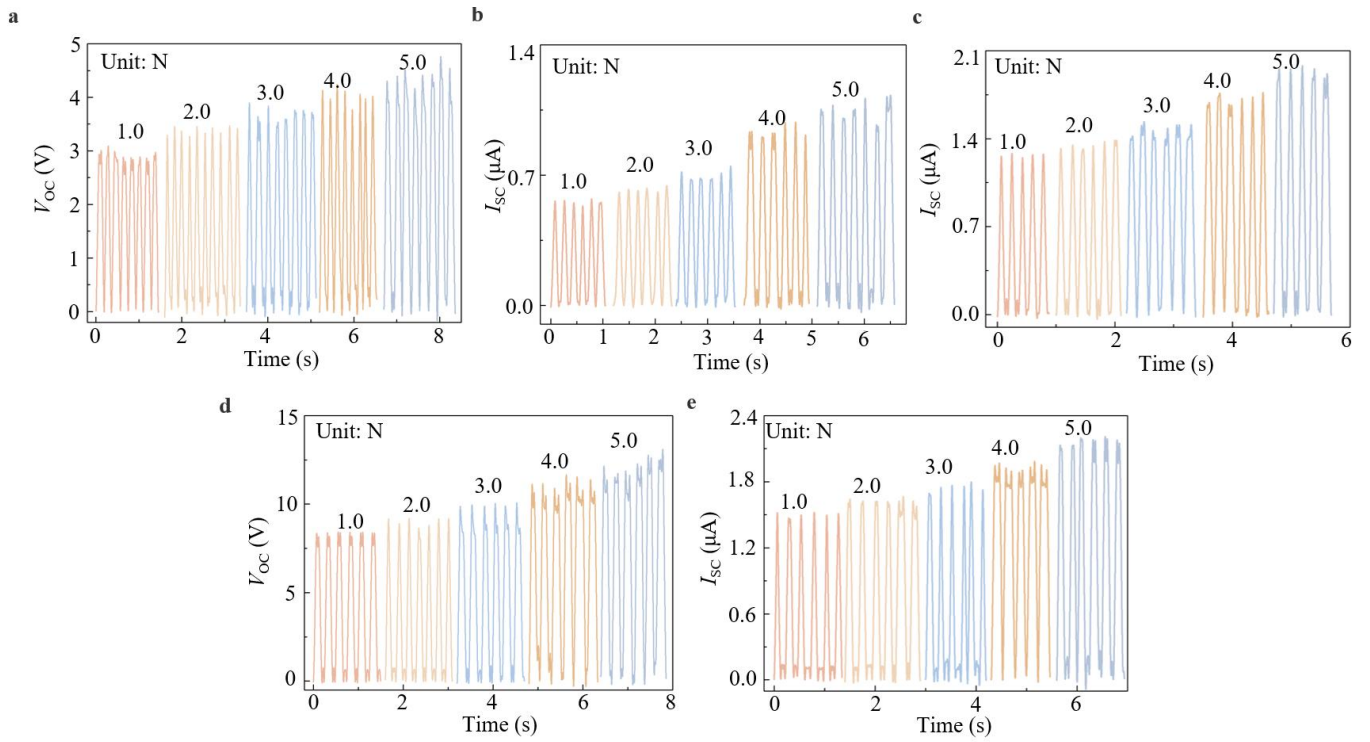


Fig. S13 Open-circuit voltage and short-circuit current output of the ES-MNP with different concentrations under varying pressure conditions. **a, b** HA/G-5% IL/PEDOT:PSS. **c** Short-circuit current of the HA/G-10% IL/PEDOT:PSS. **d, e** HA/G-15% IL/PEDOT:PSS.

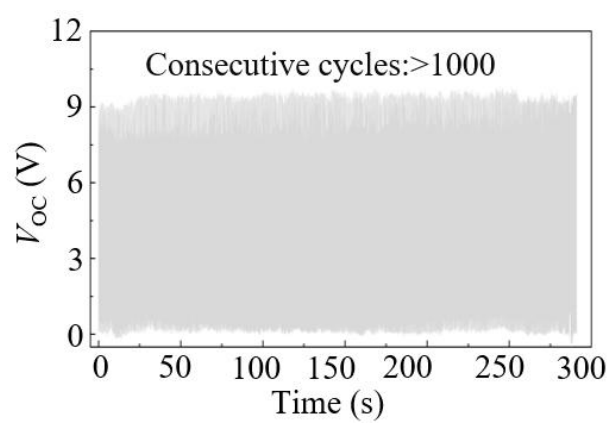


Fig. S14 Stability evaluation of electrical output for the ES-MNP during about 1000 consecutive cycles.

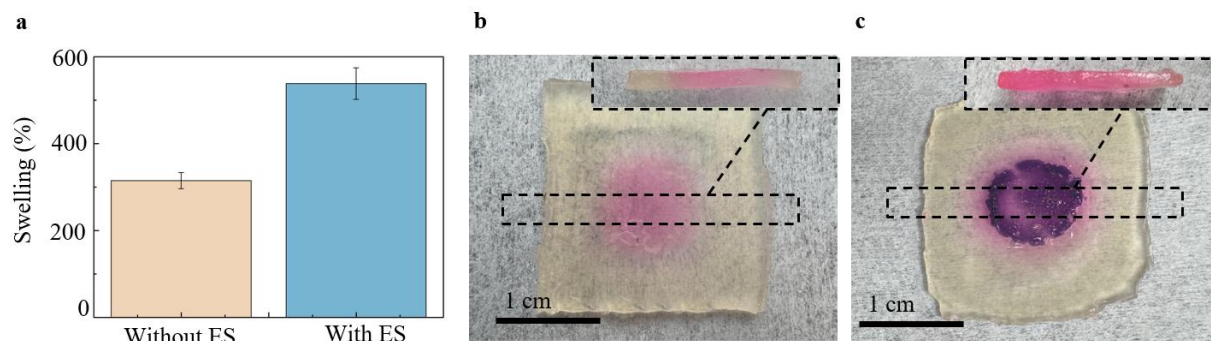


Fig. S15 Visual characterization of the TENG-driven drug release mechanism. **a** Comparison of the swelling ratio of drug-loaded patches with and without ES. Optical images showing RhB diffusion into gelatin hydrogel **b** without ES and **c** with ES. Insets: cross-sectional images. Data in **a** were presented as means $\pm$ SD, $n = 3$.

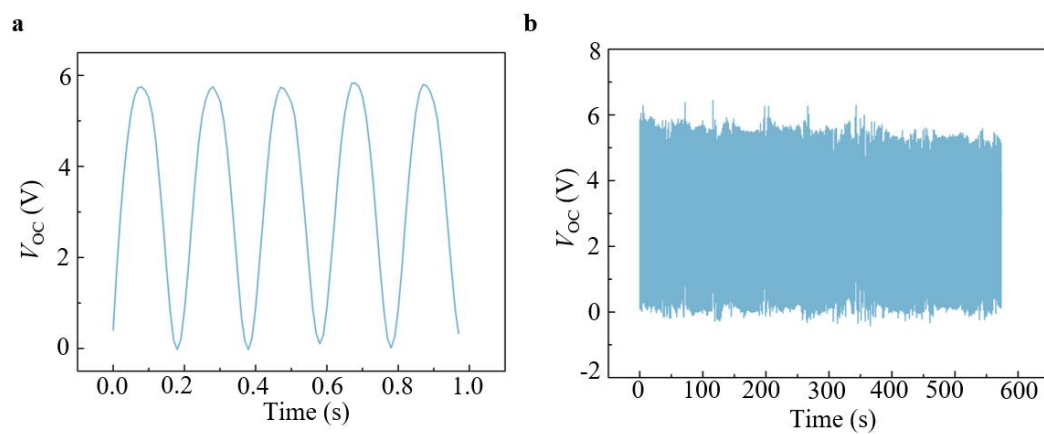


Fig. S16 Open-circuit voltage under electrically stimulated drug release. **a** Actual electrical output during the release phase. **b** Output stability over 2000 consecutive release cycles.

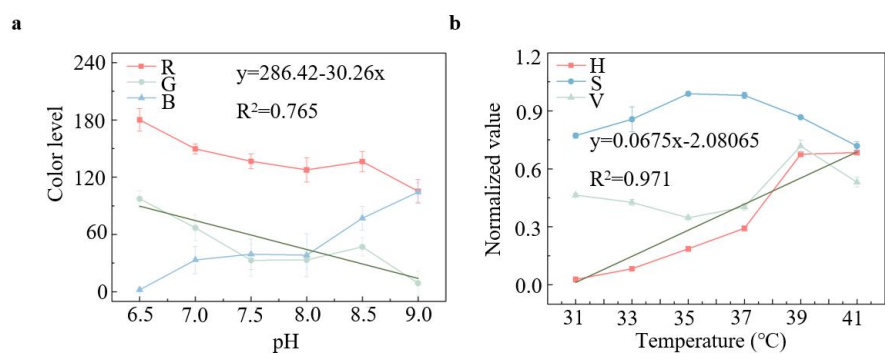


Fig. S17 Statistical analysis of changes in RGB and HSV, corresponding to **a** pH and **b** temperature levels. The straight lines were the linear fitting lines of the G value and Hue value. Data in **a** and **b** were presented as means $\pm$ SD, $n = 3$.



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178 **Fig. S18** Image of the SPMNP at the wound site.
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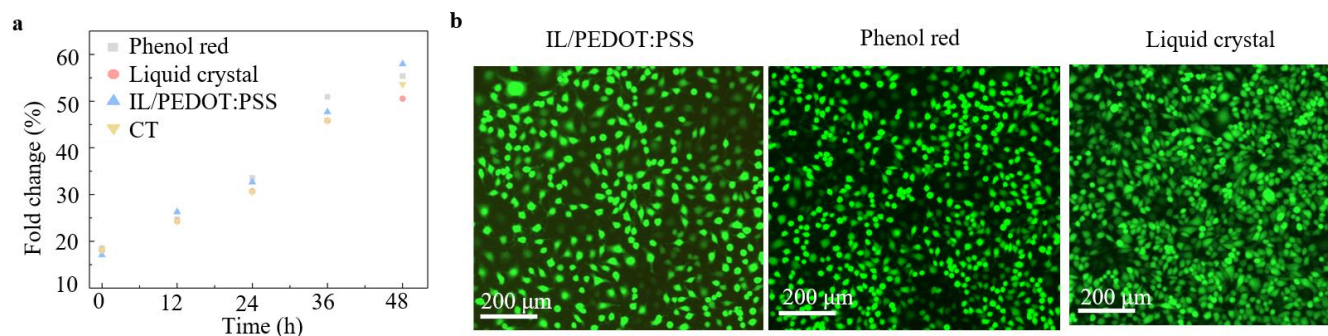


Fig. S19 Biocompatibility evaluation. **a** Comparison of cell proliferation effects across different samples at 48 h. **b** Fluorescent microscopy images of live/dead staining after 48 h of cell seeding on different sample groups.

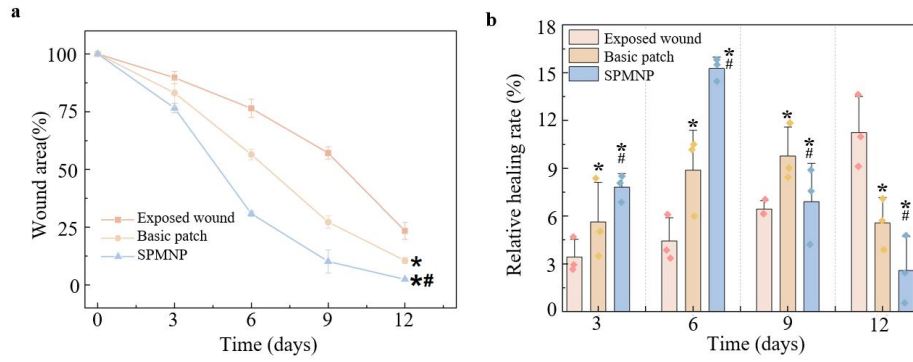


Fig. S20 Quantitative analysis of **a** wound area and **b** relative healing rate for each group on days 0, 3, 6, 9, and 12. ($n = 3$ independent samples. $*p < 0.05$. * and # indicate the significant differences between other groups, respectively. All statistical analyses were performed by one-way ANOVA. Data were presented as means $\pm$ SD).

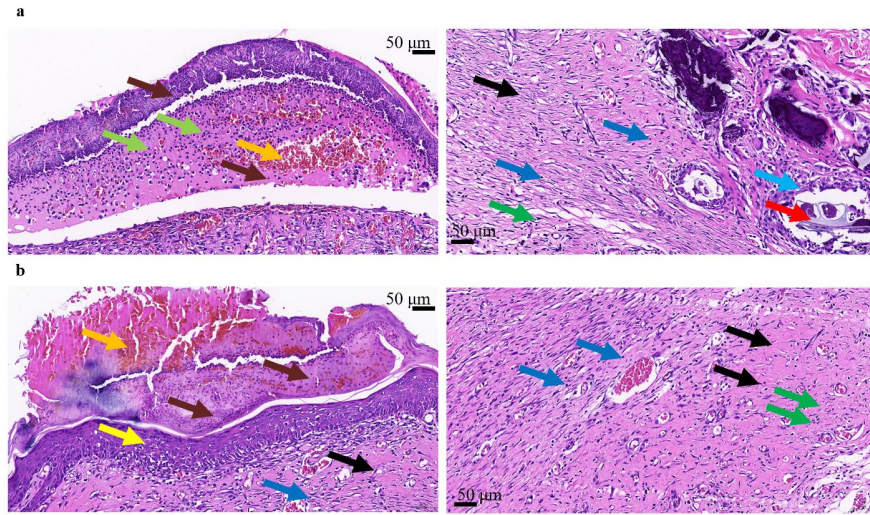


Fig. S21 Detailed histological analysis of wound healing tissue showing cellular and structural components. **a, b** H&E staining reveals comprehensive wound healing characteristics without ES and with ES groups. Necrotic cell debris and eosinophilic material (brown arrows), mild hemorrhage (orange arrows), mild acanthosis of spinous layer (yellow arrows), fibrous connective tissue proliferation (black arrows), neovascularization (green arrows), and inflammatory cell infiltration (blue arrows).