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Quasi-BIC metasurfaces enable rapid, localized singlet-oxygen generation

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Abstract

Bound states in the continuum (BIC) provide a photonic route to concentrate and store electromagnetic energy with minimal radiative leakage. Here, we report Au–TiO₂ metasurfaces that couple q-BIC optical resonance to interfacial charge transfer, enabling hot-carrier-mediated generation of ¹O₂ within subwavelength optical paths. Photonic engineering acts through two cooperative effects: (i) increased optical absorption that boosts hot-carrier generation at the Au/TiO₂ interface; and (ii) ultralow noble-metal loading that suppresses electron–hole recombination at metal/semiconductor junctions, thereby prolonging carrier lifetimes. These effects jointly yield a synergistic enhancement of ¹O₂ production beyond either pathway alone. Under continuous-wave excitation, the metasurfaces reach a local molar-level concentration of ¹O₂ within seconds, corresponding to an approximately six-order-of-magnitude increase in local ¹O₂ concentration compared with conventional approaches. Tuning structural asymmetry and excitation wavelength enables wavelength- and position-selective cytotoxicity without additional molecular sensitizers. By decoupling strong absorption from noble-metal usage while extending hot-carrier persistence in a single platform, BIC-engineered metasurfaces offer a general way to achieve efficient photon-to-chemical conversion at solid–liquid interfaces. This approach is of significant value to rapid-acting photodynamic therapy, selective oxidation, and flow microreactors where low dose and geometric precision are critical.

Introduction

Singlet oxygen (¹O₂), the lowest excited electronic state of molecular oxygen^{1–4}, serves as one of critical reactive species in photodynamic therapy^{5,6}, photocatalytic oxidation^{7,8}, and advanced environmental remediation⁹. Conventional ¹O₂ generation relies on molecular photosensitizers, such as porphyrins¹⁰ and xanthene¹¹ dyes, that undergo Type II energy transfer upon photoexcitation^{12,13}. While these organic systems achieve moderate quantum yields, they suffer from wavelength-nonspecific activation, rapid photobleaching, and poor biocompatibility—factors that necessitate recurrent dosing and limit clinical precision^{14–16}.

Recent advances in nanophotonics employ metallic and semiconductor nanostructures as alternative

sensitizers^{17–20}, yet their ¹O₂ yields remain orders of magnitude below therapeutic thresholds due to fundamental limitations in carrier dynamics and photon management²¹. Metallic nanoparticles leverage localized surface plasmon resonances (LSPRs) to concentrate light into subwavelength volumes, generating hot carriers that can drive oxygen activation^{22–25}. However, ultrafast electron-hole recombination (<100 fs) in noble metals restricts catalytic turnover rates. Semiconductor nanoparticles such as titanium dioxide (TiO₂) possess a bandgap that reduces electron-hole recombination to some extent, yet their singlet oxygen (¹O₂) quantum yield still remains very low, and ultraviolet excitation is required, which is fundamentally incompatible with biological tissues^{26–28}. Hybrid metal-semiconductor architectures can enhance carrier lifetimes through the Schottky barrier, which effectively suppresses hot electron recombination^{29–31}. However, they face a challenging material trade-off: increasing the metal content enhances visible-light absorption and boosts the number of activated carriers, but it also introduces additional

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recombination centers, thereby reducing carrier lifetimes. On the other hand, designs with reduced metal content sacrifice photon absorption efficiency, thereby limiting the number of separated carriers. This trade-off confines practical $^1\text{O}_2$ concentrations to sub-micromolar levels, which is generally insufficient for targeted therapeutic or catalytic applications^{17,18,32,33}.

Bound states in the continuum (BIC) represent a unique class of non-radiative electromagnetic modes that coexist with propagating waves in periodic photonic structures^{34–38}. Originating from symmetry-protected destructive interference and governed by symmetry- and topology-protected singularities in momentum space, these states exhibit exceptional light confinement capabilities by suppressing energy leakage through radiation channels³⁹. When implemented in dielectric metasurfaces, BICs focus optical energy into deeply sub-wavelength volumes, which sharply increases the interaction between light and matter^{40–42}, creating localized electromagnetic hotspots ideal for driving nanoscale photochemical processes^{43–46}. This light-trapping mechanism functions independently of material absorption, providing new opportunities to simultaneously enhance carrier generation and optimize carrier separation efficiency in catalytic systems⁴⁷.

We report Au-TiO₂ metasurfaces that couple q-BIC optical resonance to interfacial charge transfer, enabling rapid, hot-carrier-mediated generation of $^1\text{O}_2$ within a subwavelength optical path and with ultralow noble-metal loading (Fig. 1a). Resonant field confinement boosts absorption while mitigating recombination; the metasurface with the optical thickness of ~100 nm achieves ~45% optical absorption at the wavelength of 532 nm. This enables a local molar-level $^1\text{O}_2$ concentration within seconds, corresponding to an approximately six-order-of-magnitude increase over conventional approaches. Time-correlated single-photon counting of the 1270 nm phosphorescence with spectral filtering validates $^1\text{O}_2$ emission, and complementary frequency-domain analyses together with thermal controls isolate its photochemical origin from photothermal backgrounds. Tuning structural asymmetry and excitation wavelength realizes wavelength- and pixel-level selectivity, enabling rapid, sensitizer-free cytotoxicity. Collectively, these design principles decouple strong absorption from noble-metal usage and offer a general way to achieve efficient light-to-chemical conversion at solid-liquid interfaces.

Results

Mechanism of singlet oxygen generation via BIC-enhanced metasurface

We adopt a critical-coupling strategy built on q-BIC control to maximize interfacial absorption in an ultrathin Au-TiO₂ metasurface. The unit cell (Fig. 1b) comprises

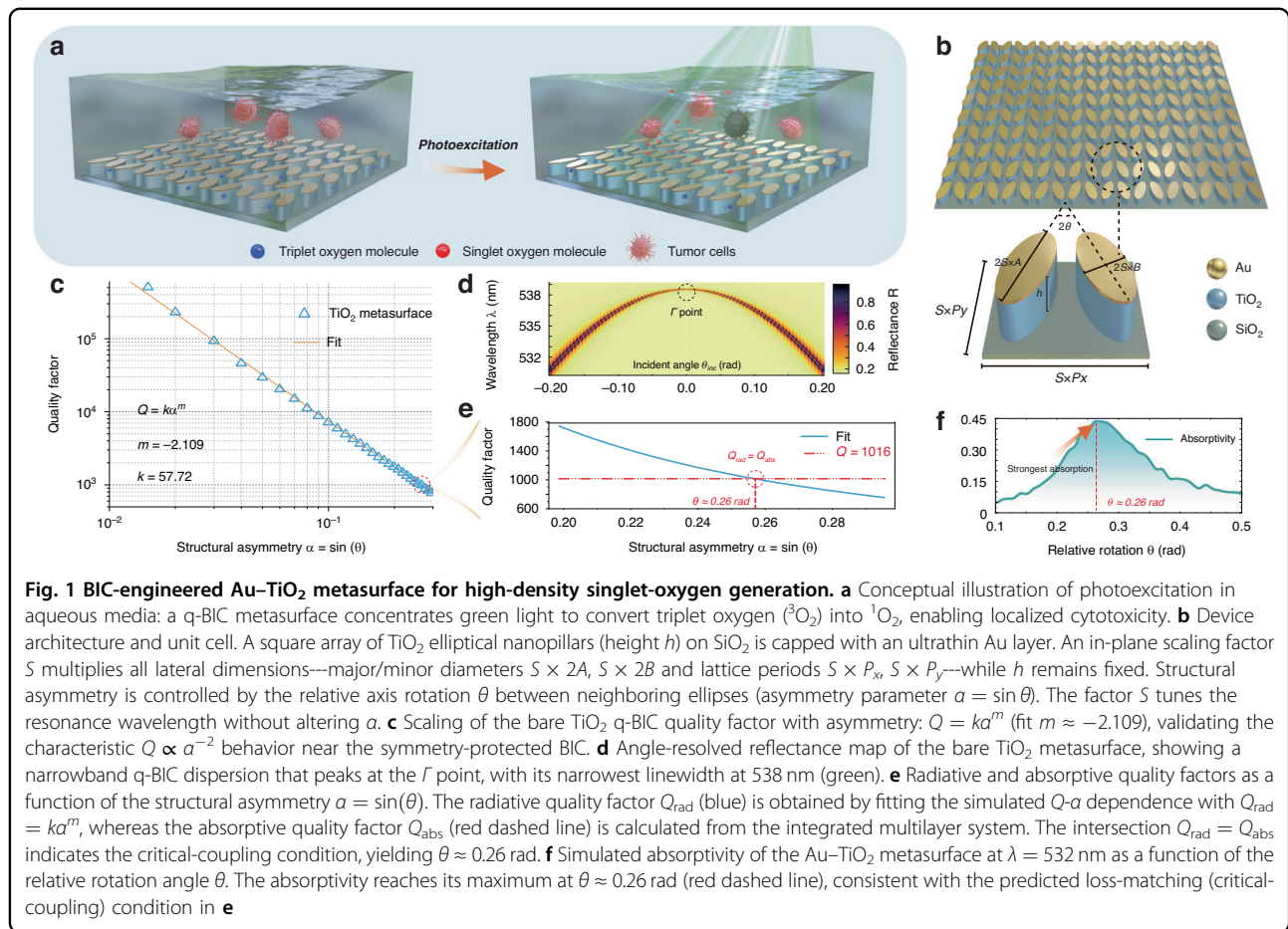
TiO₂ elliptical nanopillars of height $h = 100$ nm on SiO₂, capped with a 7 nm Au layer. A weak in-plane symmetry breaking, implemented by a relative rotation θ between neighboring ellipses (asymmetry parameter $\alpha = \sin \theta$), lifts the symmetry protection and converts the BIC into a radiative q-BIC. The bare (Au-free) dielectric array exhibits the expected $Q \propto \alpha^{-2}$ scaling (Fig. 1c) and a narrowband dispersion with a maximum at the Γ -point at 538 nm (Fig. 1d). Introducing the ultrathin Au film opens an absorptive channel. We then tune the asymmetry (rotation angle θ) to continuously modulate the radiative leakage and identify the critical-coupling point by the condition $Q_{\text{rad}} \approx Q_{\text{abs}}$ ^{48,49}, which occurs at $\theta \approx 0.26$ rad (Fig. 1e and Supplementary Text 1). At this point, the interfacial absorptance reaches its maximum, yielding ~45% at $\lambda = 532$ nm within an optical thickness of ~100 nm (Fig. 1f).

The optical response directly governs hot-carrier dynamics at the Au/TiO₂ interface. Near-field simulations confirm an E_x -polarized dipolar q-BIC mode (Fig. 2a), and the heterojunction exhibits a narrow absorptivity band pinned to the q-BIC wavelength, which exceeds that of a standalone 7 nm Au film (Fig. 2b). The near-field enhancement at the maximum absorption condition is shown in Fig. 2c, where the optical energy is strongly localized at the rims of the Au nano-ellipses and also penetrates into the underlying TiO₂ pillars (peak $|E|/|E_0| \approx 14$). Consistent with this energy localization, two-temperature modeling further predicts rim-localized electron heating within the Au nano-ellipses (Fig. S2). In the Schottky-junction picture (Fig. 2d), BIC-enhanced absorption broadens the electron distribution and enables emission of hot carriers over the barrier $\Delta\phi \approx 0.8$ eV from Au (E_F) into the TiO₂ conduction band (E_C)^{50,51}, thereby initiating interfacial redox steps that form $^1\text{O}_2$. By design, BIC photonic engineering localizes the optical field and absorption at the metal rim, enabling the same radiative energy to be absorbed with a substantially smaller amount of metal (Fig. 2e and Supplementary Text 2).

The use of smaller metallic volumes to achieve higher light absorption for $^1\text{O}_2$ generation shows two significant benefits: (i) By enhancing light absorption per unit volume of the metal, the system increases electron activity, which can be quantified by electronic temperature (T_e)⁵², thereby improving catalytic efficiency. (ii) Ultralow metal loading mitigates the recombination loss and extends carrier lifetime, thereby enhancing photocatalytic performance.

Our photonically engineered heterostructure outperforms conventional metal-semiconductor hybrids—including near-perfect absorbers⁵³, Au-TiO₂ nanospheres⁵⁴, Au-CdS nanoparticles⁵⁵, and arbitrary-radius nanostructures^{56,57}—in decoupling metal loading from optical absorptance (Fig. 2f).





For the equivalent absorbed laser power, the significant reduction in gold volume indicates strong light-matter interactions, leading to a substantial increase in electron temperature (*T_e*). The relationship between *T_e* and hot-carrier generation efficiency (*J_{th}*) is expressed as⁵⁸:

$$J_{th} \propto T_e^2 \exp\left(\frac{-q\phi_B}{k_B T_e}\right) \quad (1)$$

where *qφ_B* = 0.8 eV and *k_B* is the Boltzmann constant. When the 532 nm *E_x*-polarized illuminates the metasurface at the focused spot size of 10 μm and the power of 25 mW (*S* = 1.108, *θ* = 0.26 rad), the heterojunction generates a photocurrent of 2.6 pA—a 6.2-fold enhancement over the 0.42 pA produced by conventional Au–TiO₂ nanoparticles under identical excitation conditions (Supplementary Text 3).

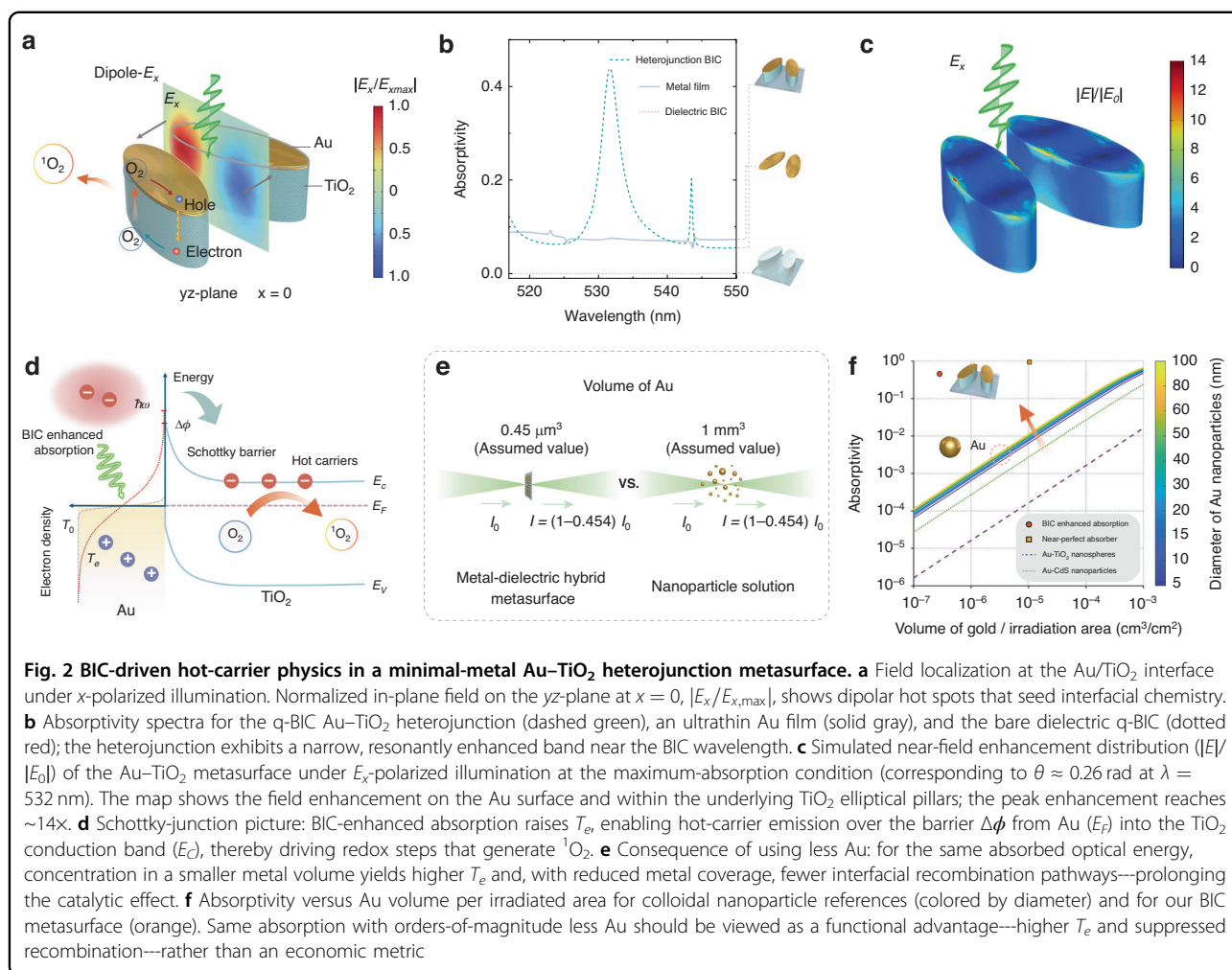
While the photocurrent magnitude differs by a factor of 6.2 between the two approaches, the spatial distribution of current generation shows a fundamentally distinct behavior. In the nanoparticle system, the photocurrent constitutes the sum of microcurrents generated by individual particles dispersed throughout the macroscopic aqueous

solution. In contrast, photocurrent generation in the metasurface is highly localized, occurring exclusively within the irradiated region. This spatial confinement enables rapid catalytic conversion of oxygen molecules within micrometer-scale proximity to the metasurface. Combined with the exceptional adsorption capacity of TiO₂, this configuration produces high ¹O₂ concentrations in the immediate vicinity⁵⁹. This q-BIC metasurface establishes synergistic interplay among photonic energy localization, hot electron dynamics, and surface adsorption processes to achieve catalytic enhancement.

Fabrication and parameter characterization of metasurfaces

The q-BIC metasurface is fabricated using micro-nano processing technology (Fig. 3a and Supplementary Text 4). (1) A layer of electron beam resist (polymethyl methacrylate) is coated on a glass substrate, and a thin layer of aluminum is deposited at the bottom of the resist layer to improve conductivity. (2) The resist layer is patterned and subsequently developed using electron beam lithography at 8 C/m², 0.8 nA, and 80 kV. (3) A 100 nm TiO₂ layer and a 7 nm Au layer are deposited on the imaged resist layer





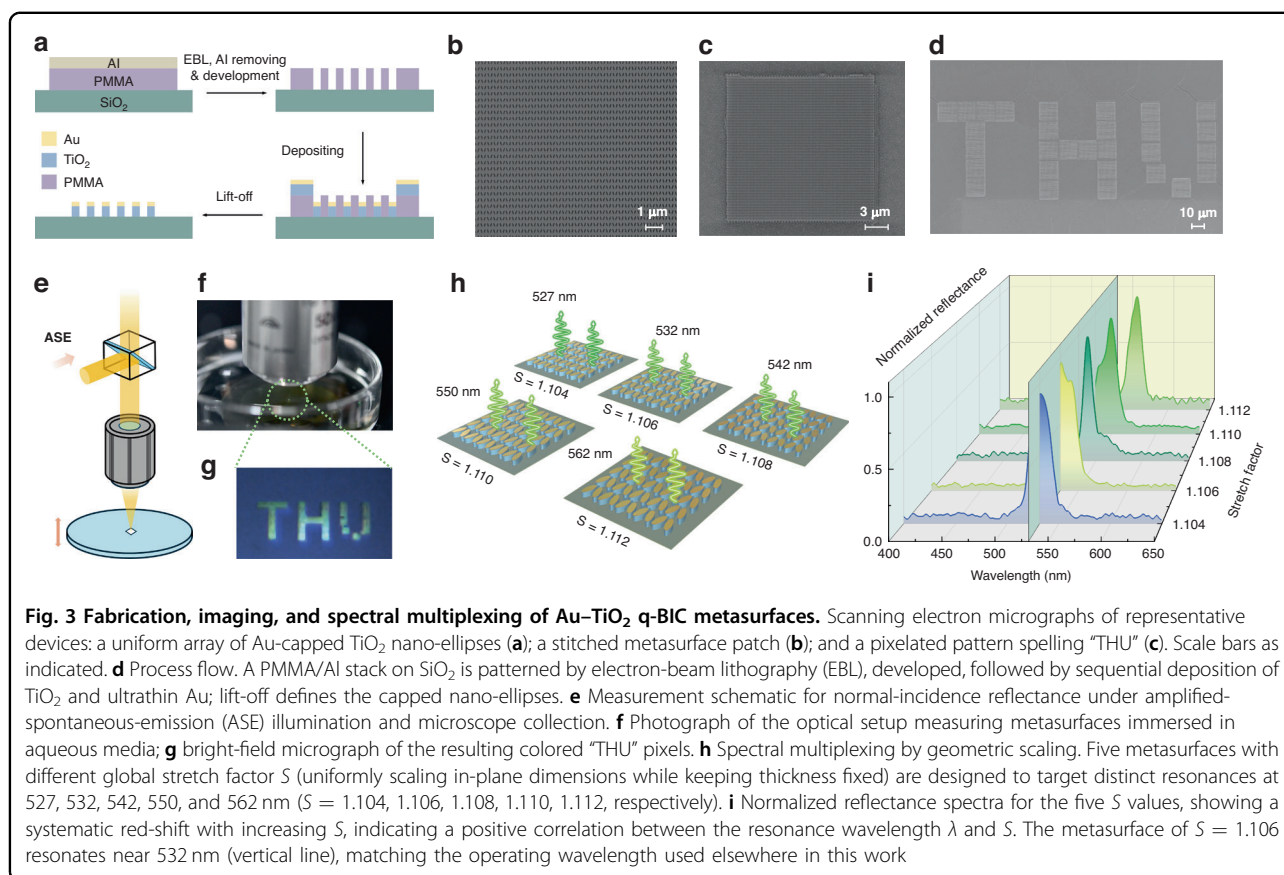
using electron beam evaporation. (4) During the stripping process, the sample is immersed in acetone for 12 hours to remove TiO₂ and Au in the unexposed areas. After completion, the metasurface is characterized by scanning electron microscopy (Fig. 3b–d).

BIC optical metasurfaces typically exhibit complementary spectral features that include absorption at a specific wavelength and a corresponding reflection peak at nearly the same wavelength. We utilize this phenomenon to precisely characterize the resonant behavior of our metasurface through reflection spectroscopy. The fabricated metasurface is immersed in deuterated water (D₂O), and a collimated amplified spontaneous emission (ASE) supercontinuum laser is focused on the patterned substrate (Fig. 3e). We optimize the interaction between the beam and the sample by vertically translating the substrate to align the beam waist with the metasurface plane. Since the optimized BIC mode is supported by the E_x polarization, a custom achromatic half-wave plate is used to precisely control the polarization direction perpendicular to the elliptical

symmetry axis (transverse polarization), which is crucial for activating the q-BIC mode.

Our custom-built optical microscopy system enables precise positioning of the ASE beam on the metasurface. After optimized focusing, strong green reflectance is visually observed (Fig. 3f), with the fabricated THU-shaped pattern (Fig. 3d, g) confirming the designed resonance. To accommodate inevitable nanofabrication errors, we fabricate a sample comprising five metasurfaces with different structural parameters ($S = 1.104\text{--}1.112$, Fig. 3h). Hyperspectral imaging is performed using the same microscopy system to capture the reflection spectra of each sample (Fig. 3i). The measured reflection peaks show good agreement with simulations. The moderate broadening likely arises from a combination of (i) fabrication-induced dimensional variations among individual resonators and (ii) the finite angular spectrum introduced by the objective of high numerical aperture. The metasurface with $S = 1.106$ demonstrates optimal resonance at 532 nm and is subsequently selected for $^1\text{O}_2$ generation experiments. The absorbance of the metasurface in aqueous





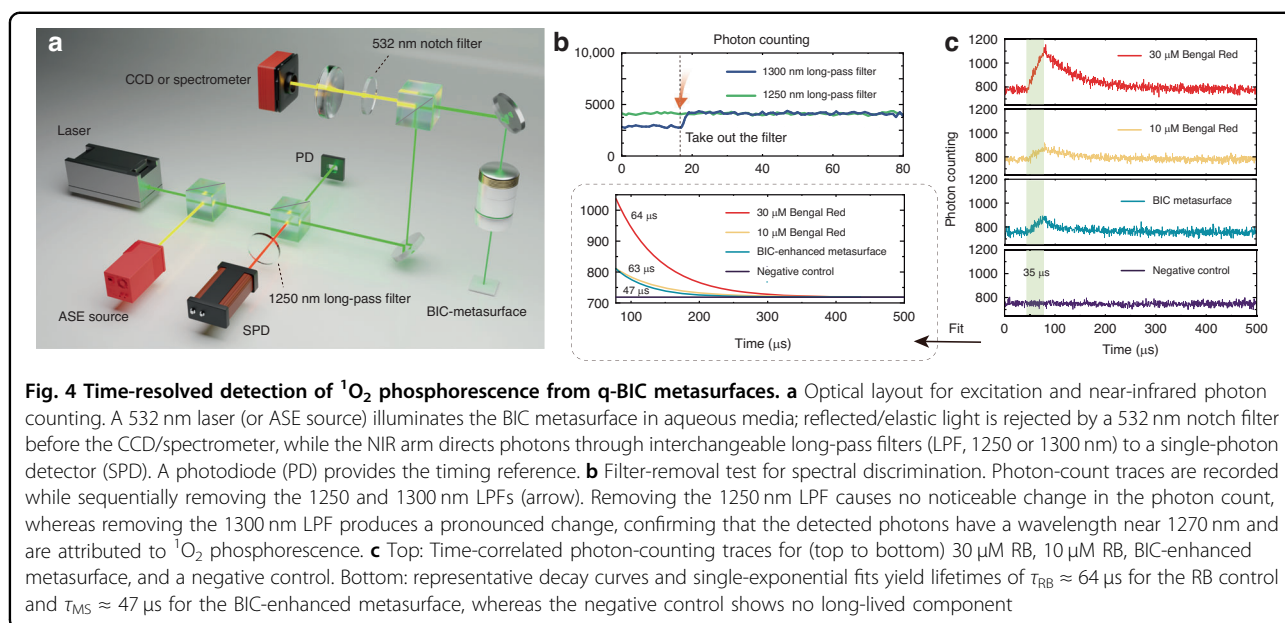
solution is obtained from energy conservation, $A = 1 - R - T$, where R and T are the measured specular reflectance and transmittance of the metasurface, respectively. Experimentally, R and T are determined under 532 nm pulsed-laser excitation using a photodetector (PD) and an oscilloscope by reading the pulse peak amplitude as a linear proxy for optical intensity. For the reflectance measurement, a 50:50 non-polarizing beamsplitter is used and the reflected-signal increment is corrected by a factor of two, while background reflections from the deuterated water surface and the glass vessel are subtracted. For the transmittance measurement, the transmitted signal is recorded directly under the same focusing and collection conditions. The patterned region is compared against an unpatterned area measured in the same optical configuration as a reference. Using this procedure, we obtain $A \approx 0.45$ at 532 nm, consistent with numerical simulations.

Steady-state singlet oxygen generation

To investigate the $^1\text{O}_2$ production dynamics of the BIC metasurface in steady-state operation, we perform time-resolved phosphorescence measurements in oxygen-saturated deuterium oxide (D_2O)⁶⁰. A pulsed 532 nm laser (pulse width of 35 μs , repetition rate of 2 kHz) is used to activate the metasurface, and the $^1\text{O}_2$

phosphorescence signal at 1270 nm is detected using time-correlated single photon counting. Long-pass filters (LPFs) and monochromators are employed to eliminate scattered excitation light, ensuring precise lifetime measurements (Fig. 4a). Unless otherwise stated, all kinetic curves are acquired under a fixed incident optical power (25 mW) at the sample plane (i.e., constant incident photon flux). We validate the phosphorescence wavelength by temporarily removing LPFs with different cutoff wavelengths (1250 and 1300 nm) and monitoring the photon counts; the pronounced change upon removing the 1300 nm LPE, together with the negligible change upon removing the 1250 nm LPE, indicates that the emission is primarily confined to 1250–1300 nm, consistent with the characteristic $^1\text{O}_2$ phosphorescence near 1270 nm (Fig. 4b).

The phosphorescence decay profiles further confirm that this metasurface with sub-micron optical path (100 nm) achieves $^1\text{O}_2$ emission intensity comparable to macroscopic photosensitizer solutions (10 μM Rose Bengal aqueous solution with the optical path as long as 10 mm, Fig. 4c). We chose 10 μM RB as a representative benchmark concentration because increasing the concentration of conventional molecular photosensitizers does not increase singlet oxygen output, owing to



concentration-dependent self-quenching/aggregation effects^{61,62}. Specifically, the $^1\text{O}_2$ phosphorescence counts from 10 μM Rose Bengal (RB) solution (yellow curve) and from the metasurface (blue curve) exhibit identical peak amplitudes in temporal fitting (Fig. 4c). The measured $^1\text{O}_2$ lifetime for the BIC metasurface is 47 μs , which is shorter than the 63 and 64 μs lifetimes observed for 10 μM and 30 μM RB solutions, respectively. This reduction in lifetime is attributed to the elevated local oxygen concentration near the TiO_2 surface, where oxygen adsorption significantly enhances the quenching of $^1\text{O}_2$ ^{63–65}. The local $^1\text{O}_2$ concentration at the metasurface interface reaches approximately 1.12 M as calculated (Supplementary Text 5), which is 10^6 times higher than the $^1\text{O}_2$ concentrations achieved by traditional photosensitizer-based methods ($\sim 0.87 \mu\text{M}$ from RB aqueous solution). This concentration is primarily due to TiO_2 's strong oxygen adsorption and the photonic enhancement provided by the metasurface.

The wavelength-specific nature of $^1\text{O}_2$ nanogenerator is further confirmed by varying the structural parameter S . Metasurfaces with $S = 1.104$ and $S = 1.106$ exhibit significantly higher $^1\text{O}_2$ photon counts relative to the baseline (negative control), while metasurfaces with $S \geq 1.108$ show no detectable activity (Fig. S3c). This strong dependence on the q-BIC resonance highlights the critical role of photonic mode engineering in driving efficient $^1\text{O}_2$ generation.

Temporal evolution of singlet oxygen generation

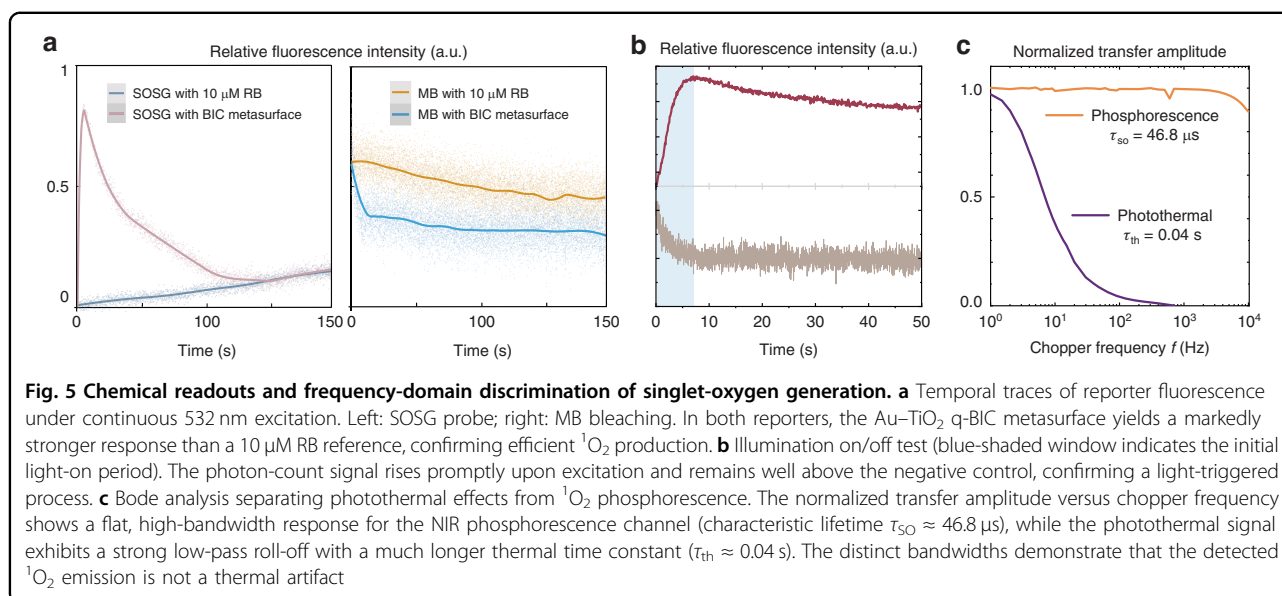
To investigate the temporal evolution of $^1\text{O}_2$ generation, we employ singlet oxygen sensor green fluorescent probe (SOSG)⁶⁶, a highly selective fluorescent probe that reacts

specifically with $^1\text{O}_2$ to form SOSG-ep while emitting green fluorescence. Under identical conditions with constant incident photon flux, both the BIC metasurface and a 10 μM RB photosensitizer solution are illuminated while monitoring SOSG fluorescence changes to infer $^1\text{O}_2$ generation (Fig. 5a, left). The metasurface exhibits a rapid fluorescence intensity rise within the initial 8 seconds, demonstrating enhanced $^1\text{O}_2$ generation kinetics surpassing conventional photosensitizer solutions. This accelerated dynamics is attributed to the prioritized activation of oxygen molecules adsorbed on TiO_2 through photoinduced carrier transfer.

Under laser illumination of the RB solution, $^1\text{O}_2$ is produced throughout the entire illuminated region. In contrast, when the laser is focused on the metasurface, the generation of $^1\text{O}_2$ is confined to within a diffusion length of only a few hundred nanometers ($\sim 800 \text{ nm}$) above the patterned region. Although the total number of $^1\text{O}_2$ molecules generated in the RB solution and metasurface may become comparable over extended irradiation times (Fig. 5a, left), the distinct volumes in which they exist result in significantly different concentration profiles (Fig. S4). The fluorescence intensity from BIC metasurface then gradually decreased after the peak at 8 s, which can be attributed to the conversion of $^1\text{O}_2$ into superoxide anions (O_2^-) that subsequently desorb from the TiO_2 surface⁶⁷. This transformation signifies the completion of the catalytic cycle, where $^1\text{O}_2$ activation leads to oxygen molecule dissociation and regeneration of active sites.

To further confirm the photocatalytic activity of the metasurface, methylene-blue (MB) degradation experiments are conducted (Fig. 5a, right)¹². Under identical illumination conditions, the metasurface demonstrates





faster MB degradation compared to the 10 μM RB solution, validating its superior photocatalytic performance. The enhanced degradation rate correlates with the accelerated ¹O₂ generation observed in the SOSG experiments. A direct comparison of the temporal behavior of SOSG fluorescence and MB degradation (Fig. 5b) reveals that the two processes exhibit consistent kinetic profiles under illumination. This temporal alignment reflects the ultrafast generation of ¹O₂ by the metasurface immediately after the onset of illumination, providing valuable insights into the dynamics of photonic-enhanced reactive oxygen species (ROS) production in the early stages of light activation.

To exclude the possibility that photothermal effects produce ¹O₂, we performed a compact frequency-domain discrimination by modulating the pump light and comparing the normalized transfer amplitudes of the NIR phosphorescence (1270 nm band) with those of the metasurface reflectance measured by a photoelectric detector (Fig. 5c). The phosphorescence exhibits a flat, high-bandwidth response consistent with the micro-second lifetime of ¹O₂, whereas the reflectance shows a strong low-pass roll-off with a thermal time constant on the order of 10⁻² s. The clear bandwidth separation confirms that the detected 1270 nm emission is photochemical rather than photothermal.

Evaluation of the ability of metasurfaces to induce death in cells

Under short-term laser irradiation, the concentration of ¹O₂ generated by photosensitizers dispersed in aqueous environments is generally insufficient to induce cell death, as the threshold concentration required for cell death is approximately in the millimolar range²¹. Achieving higher

¹O₂ concentrations requires increasing photosensitizer dosage and extending laser exposure times to several hours. However, excessive photosensitizer levels pose significant toxicity to biological tissues, limiting their biomedical applications^{68,69}, and prolonged irradiation significantly increases patient pain^{70,71}. Notably, BIC metasurfaces introduced here effectively overcome these limitations, having the ¹O₂ concentration rapidly reaching to molar level within 10 s.

To investigate the cytotoxicity of q-BIC metasurfaces through ¹O₂ generation, we conducted in vitro experiments using U2OS human osteosarcoma cells cultured directly on metasurface substrates⁷². The substrate comprises a circular SiO₂ wafer with three identical metasurface modules, each containing parametric arrays defined by geometric parameters (Fig. S6).

A 532 nm expanded laser beam (diameter: 2.5 mm, power: 25 mW) uniformly irradiates each metasurface module. Post-exposure samples are incubated for 6 h to allow death progression, with cell death assessed by Calcein-AM/PI dual staining. Apoptotic cells are mainly localized around metasurface-patterned regions $S = 1.104$ and $S = 1.106$ (Fig. 6, Panels V and VIII). Dose-response analysis reveals time dependence: increasing exposure duration from 75 to 125 s enhances ¹O₂ generation, correlating with elevated cell mortality.

This spatial selectivity aligns with spectral response mapping (Fig. 3h), where regions of $S = 1.104$ and $S = 1.106$ exhibit stronger 532 nm resonance than regions of $S = 1.108$ – 1.112 , demonstrating the localized cytotoxicity. To validate wavelength specificity, the 532 nm laser is replaced with a 562 nm light source (25 mW, 125 s exposure), which induces significant cell death near region of $S = 1.112$ (Fig. 6a, Panel XI), corresponding to



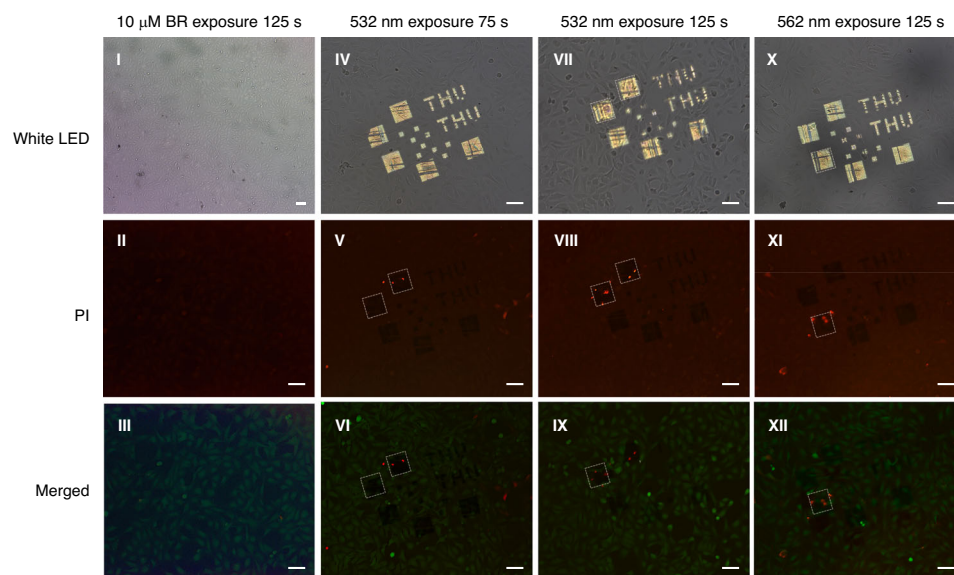


Fig. 6 Wavelength-selective, pixel-resolved photocytotoxicity on Au-TiO₂ q-BIC metasurfaces. Cells were cultured directly on patterned metasurfaces and imaged in three channels: *White LED* (bright field, top row), *PI* (propidium iodide; dead, middle row), and *Merged* (Calcein-AM/PI overlay; live/dead, bottom row). Columns (left to right): **I–III** 10 μ M RB control, 125 s exposure; **IV–VI** 532 nm irradiation for 75 s; **VII–IX** 532 nm for 125 s; **X–XII** 562 nm for 125 s. Dashed boxes mark representative metasurface pixels used for comparison. Under 532 nm illumination (**IV–IX**), PI-positive cells concentrate in resonance-mapped zones corresponding to designs scaled to $S = 1.104$ and $S = 1.106$; surrounding, off-resonant regions retain Calcein fluorescence. When the excitation is shifted to 562 nm (**X–XII**), cell death localizes to pixels red-tuned to $S = 1.112$, consistent with spectral matching. Scale bars, 10 μ m. Together, these data demonstrate spatially selective, resonance-matched photodynamic cytotoxicity arising from localized singlet-oxygen generation

the 562 nm reflectance peak. In contrast, using 10 μ M RB in Hank's balanced salt solution (HBSS) buffer under equivalent photodynamic conditions (25 mW, 125 s exposure, Fig. 6a, Panels I–III) shows no patterned cell death in laser-irradiated regions.

The above results demonstrate that q-BIC metasurfaces enable precision-targeted photodynamic therapy, with spatial resolution governed by metasurface patterns and spectral selectivity defined by engineered optical resonances. This on-demand $^1\text{O}_2$ generation technology achieves unprecedented spatiotemporal control, representing a significant advancement over traditional photosensitizer-based cell-targeting approaches.

Discussion

We have established a metasurface strategy that unites q-BIC resonance control with critical coupling to maximize interfacial absorption in a minimal-metal Au-TiO₂ architecture. By balancing radiative leakage with intrinsic loss within a subwavelength optical path, the q-BIC metasurface concentrates optical energy at Au/TiO₂ heterojunctions while maintaining ultralow noble-metal loading. The small metal volume concentrates the same absorbed power at high density, thereby elevating the electron temperature and strengthening the hot-carrier population; simultaneously, the reduced density of

metallic recombination centers suppresses carrier recombination and extends carrier persistence at the interface. This design yields strong absorption at 532 nm and promotes hot-carrier generation and longevity, enabling local molar-level $^1\text{O}_2$ within seconds and an approximately six-order-of-magnitude increase in local $^1\text{O}_2$ concentration compared with conventional approaches, providing a material-efficient route to activate interfacial redox chemistry.

Under continuous-wave excitation, near-interface photochemistry rapidly yields pixel-confined, high-density $^1\text{O}_2$, enabling on-chip spatially programmable cytotoxicity. The $^1\text{O}_2$ signal is validated by time-resolved detection of the 1270 nm phosphorescence with spectral filtering, and complementary chemical readouts (SOSG activation and MB bleaching) exhibit temporally coherent kinetics, confirming a common reactive-oxygen flux. The metasurface thereby enables wavelength- and pixel-level control of reactivity without molecular sensitizers, yielding rapid, spatially resolved cytotoxicity in cell assays.

Beyond the specific Au-TiO₂ implementation, the principles demonstrated here—q-BIC mode engineering, impedance matching via critical-coupling, and minimal-metal hot-carrier activation—can be applied to other metal/semiconductor pairs and spectral bands. In stark contrast to conventional dye sensitizers and many



nanoparticle photocatalysts that often require higher dosages and prolonged illumination and tend to be inadvertently activated by ambient light due to broadband absorption, our metasurface enables rapid build-up of highly localized $^1\text{O}_2$ with wavelength-addressable, patterned reactivity. We anticipate immediate opportunities in rapid photodynamic therapy, selective oxidation, and on-chip or flow microreactors, where sensitizer-free operation, reduced cross-talk, and low noble-metal usage are desirable. Future work will focus on extending operation to NIR excitation, optimizing interface chemistry and stability in complex media, and integrating multiplexed resonators for spatial/spectral programmability of photon-to-chemical conversion at solid–liquid interfaces.

Materials and methods

Device fabrication

Au–TiO₂ q-BIC metasurfaces are fabricated on BF33 float-glass substrates. Substrates are sonicated in acetone and ethanol for 10 min at 200 W, rinsed with deionized water, dried with N₂, and baked at 120 °C for 30 min. A 950 PMMA A4 resist is spin-coated at 3000 rpm for 45 s and baked at 180 °C for 90 s. Patterns are defined by electron-beam lithography (NB5, 80 kV, 0.8 nA, dose 8 C/m²) under high vacuum (<2.7e-8 Torr), developed in MIBK:IPA = 1:3 for 60 s, rinsed in IPA for 60 s, and dried with N₂. Films are deposited by e-beam evaporation in a PVD75 (<1e-7 Torr, 1 Å/s): 100 nm TiO₂ followed by 7 nm Au. Lift-off in acetone for 48 h yields Au-capped TiO₂ elliptical nanopillars.

Numerical modeling

A single unit cell is modeled in COMSOL Multiphysics using Floquet periodic boundary conditions in the in-plane directions and perfectly matched layers along the propagation axis. The top and bottom faces use scattering boundaries. The superstrate is deuterated water and the substrate is SiO₂. The geometry consists of a 100 nm TiO₂ pillar capped by a 7 nm Au film.

Time-correlated single-photon counting of $^1\text{O}_2$

Singlet-oxygen phosphorescence at 1270 nm is measured with a single-photon detector (Aurea Technology, SPD_NIR, 900–1700 nm) time-tagged by a time-correlated single-photon counting module (PicoQuant TimeHarp 260 NANO). Samples are excited with a pulsed 532 nm laser (pulse width of 35 μs, repetition rate of 2 kHz). Emission is collected through a Nikon TU PLAN ELWD 50×/0.60 long-working-distance objective in the same microscope path; LPFs at 1250 and 1300 nm, together with a 532 nm notch filter, block the 532 nm excitation. Removal of the 1300 nm LPF verifies that the detected signal lies within 1250–1300 nm.

Frequency-domain discrimination

The pump light is mechanically modulated with an optical chopper (Thorlabs MC2000B; modulation frequency up to 10 kHz). The amplitude transfer response of the 1270 nm phosphorescence channel is compared with a simultaneously recorded reflectance channel detected by a photodiode amplifier (Thorlabs PDA36A2; 350–1100 nm). The phosphorescence channel shows a flat, high-bandwidth response consistent with microsecond-lived emission, whereas the reflectance exhibits a pronounced low-pass roll-off with a thermal time constant of about 0.04 s, confirming a photochemical origin of the NIR signal.

Photon-flux normalization

To avoid ambiguity between incident and absorbed photon budgets, we explicitly distinguish the incident photon flux Φ_{inc} and absorbed photon flux Φ_{abs} in data analysis. The incident optical power P_{inc} is measured at the sample plane using a calibrated power meter. The corresponding incident photon flux at wavelength λ is calculated as

$$\Phi_{\text{inc}}(\lambda) = \frac{P_{\text{inc}}}{hc/\lambda} = \frac{P_{\text{inc}}\lambda}{hc} \quad (2)$$

where h is Planck's constant and c is the speed of light. When photon-flux *density* is needed, we have

$$\phi_{\text{inc}}(\lambda) = \frac{\Phi_{\text{inc}}(\lambda)}{S} \quad (3)$$

where S is the illuminated area at the sample.

The absorbed photon flux is obtained from the measured absorbance $A(\lambda)$ as

$$\Phi_{\text{abs}}(\lambda) = \Phi_{\text{inc}}(\lambda) \times A(\lambda) \quad (4)$$

and the absorbed optical power is $P_{\text{abs}}(\lambda) = P_{\text{inc}}(\lambda) \times A(\lambda)$. The absorbance is determined from reflection and transmission measurements via

$$A(\lambda) = 1 - R(\lambda) - T(\lambda) \quad (5)$$

where $R(\lambda)$ and $T(\lambda)$ are the total reflectance and transmittance (measured, e.g., with a spectrophotometer equipped with an integrating sphere). Unless otherwise stated, kinetic traces (e.g., SOSG activation, MB bleaching, and 1270 nm phosphorescence counting) are acquired and plotted under fixed incident power P_{inc} (i.e., constant Φ_{inc}). In contrast, any quantity intended to represent an intrinsic per-photon efficiency (e.g., apparent quantum-yield-type metrics) is normalized to the absorbed photon flux Φ_{abs} using the corresponding $A(\lambda)$.



Chemical reporters

SOSG stock is prepared by dissolving 100 µg reagent in 33 µl methanol (about 5 mM), then diluting to 10 µM with deionized water before applying to the metasurface under a water layer. A non-patterned area with 10 µM RB serves as a blank, and four samplings are averaged. An MB working solution is prepared at 10 µM. MB bleaching and SOSG fluorescence are recorded under continuous 532 nm excitation in the same microscope to track $^1\text{O}_2$ dynamics.

Cell culture and phototoxicity

U2OS human osteosarcoma cells are cultured directly on the metasurface at 37 °C in a CO₂ incubator. Experiments start after the cell adhesion. Live/dead staining reagents (Calcein-AM and propidium iodide, PI) are added, and the cells are incubated for 6 h. The entire patterned area is then irradiated by a 532 nm (or 562 nm) laser for the indicated duration, after which the cells are returned to the incubator for an additional 30 min. Cell death is assessed on a fluorescence microscope (Olympus BX53M) using an Olympus U-HGLGPS 130 W fiber-coupled fluorescence light source for excitation.

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Author contributions

R.L. and X.F. conceived the idea and designed the optical metasurface. L.L. performed the COMSOL numerical simulations and patterned the TiO₂-coated substrates using electron-beam lithography. R.L. deposited the Au-TiO₂ films by electron-beam evaporation, built the fluorescence and phosphorescence detection setup, prepared the experimental reagents, and acquired the data. X.Q. cultured cells on the metasurfaces and ensured adhesion. X.Q. and R.L. carried out the theoretical analysis of the results. R.L. analyzed the experimental data and wrote the manuscript. X.F. and Q.L. guided the experiments, supervised the project, and coordinated the collaboration. All authors discussed the results and contributed to the manuscript.

Data availability

All data needed to evaluate the conclusions in the paper are present in the paper and supplementary material. Additional data related to this paper may be requested from the authors.

Conflict of interest

The authors declare no competing interests.

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