

Giant phonon-assisted upconversion photoluminescence of in situ photo-carbonized polymer dots for 3D high-definition optical disks

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Supplementary Note 1: Optical System Setups

1.1 Confocal *In Situ* Writing-Readout System

To perform high-precision *in situ* laser writing and reading of upconversion carbonized polymer dots (u-CPDs), we developed a custom confocal microscopy-based optical system (**Supplementary fig 1**). This platform was used for three-dimensional (3D) high-definition (HD) optical disk encoding in poly(ethylene glycol) diacrylate (PEGDA)-based photo-polymer thin films. The sample was mounted on a computer-controlled three-axis piezo stage (Physik Instrumente, P-563), providing sub-nanometer positioning accuracy in all spatial dimensions.

Both the writing and readout beams shared a common optical axis and objective lens, ensuring intrinsic spatial overlap between laser-written voxels and the readout focal volume, thereby eliminating registration errors during encoding and decoding. The confocal configuration suppressed out-of-focus background signals, enabling high-contrast upconversion photoluminescence (UCPL) detection from the u-CPDs.

Writing beam configuration

For writing, a 920 nm femtosecond (fs) laser (Coherent, Axon 920-1) with <150 fs pulse duration and 80 MHz repetition rate was employed. The beam was frequency-doubled using a Chameleon VUE Harmonics module via second harmonic generation to produce a 460 nm fs writing beam. Laser power was actively stabilized and continuously monitored to ensure reproducible photo-cross-linking and photo-carbonization. The beam passed through a half-wave plate and polarizer for precise power control, followed by a quarter-wave plate to generate circular polarization.

A flipping mirror directed the beam into an oil-immersion high-numerical-aperture (NA) objective lens (Olympus, UPlanApo 100×/1.5 NA), tightly focusing it into the PEGDA-based photo-polymer thin film. Lateral translation of the sample across the focal plane achieved voxel writing, while an optical shutter (Thorlabs, SH1/M) controlled exposure time, enabling deterministic formation of u-CPDs via localized photo-cross-linking and photo-carbonization.

Readout beam configuration

For UCPL readout, an 808 nm continuous-wave (CW) laser (Coherent, OBIS LX, 150 mW) excited phonon-assisted emission from the u-CPDs. The collimated excitation beam passed through a half-wave plate and polarizer for fine power adjustment, followed by a quarter-wave plate to generate circular polarization, and was focused onto the sample through the same objective lens used for writing.

Detection system

UCPL emitted by the u-CPDs was collected by the objective lens, spectrally separated from the excitation beam using a dichroic mirror (Semrock, Di03-R785-t3-25×36), and coupled into a multimode optical fiber (Thorlabs, FG050LGA). The signal was detected using a single-photon avalanche diode (SPAD, Laser Components, Count@T100-FC). A notch filter (LBTEK, ZET808NF) suppressed residual excitation light, while a short-pass filter (Semrock, BSP01-785R-25) isolated the UCPL emission band, minimizing background noise.

Resolution and voxel control

Lateral resolution was diffraction-limited by the high NA objective, enabling sub-micron voxel definition. Voxel size and UCPL intensity were jointly controlled by tuning writing laser power and exposure time, allowing deterministic grayscale encoding at the single-voxel level. Axial positioning accuracy was governed by the piezo stage, enabling precise layer-by-layer writing with micrometer-scale interlayer spacing for volumetric optical disk encoding.

This confocal platform allowed diffraction-limited writing with uniform lateral resolution and reproducible UCPL readout under low-light conditions. By tuning writing parameters, up to 1,024 grayscale levels could be encoded per voxel within the volumetric PEGDA matrix. The static confocal configuration was particularly suited for controlled experiments requiring high-fidelity single-voxel writing and readout, providing quantitative measurements of UCPL intensity, photostability, and bit-to-bit uniformity, and enabling detailed mechanistic investigations of *in situ* photo-carbonization and phonon-assisted emission in u-CPDs.

1.2 Galvo-Scanning (GS) Writing and Wide-Field Readout System

To enable ultrafast volumetric encoding of 3D HD optical disks, a GS writing system coupled with a wide-field readout configuration was developed (**Supplementary fig 2**). In contrast to point-by-point confocal writing, this architecture decouples lateral voxel positioning from mechanical stage motion, enabling high-throughput patterning over large areas while preserving sub-micron voxel fidelity.

GS writing beam configuration

A 920 nm fs laser (Coherent, Axon 920-1; <150 fs pulse duration, 80 MHz repetition rate) was frequency-doubled to 460 nm for localized polymer modification. The beam was directed through a pair of two-dimensional galvo mirrors (Thorlabs, GVS002) to achieve rapid lateral deflection. The beam passed through a half-wave plate and polarizer for precise power control, followed by a quarter-wave plate to generate circular polarization. A scan lens (Thorlabs, SL50-CLS2) combined with a tube lens

(Thorlabs, TTL200MP) minimized optical aberrations and maintained uniform focus across the scanning field (**Supplementary figs 2A, 2B, and 3A**).

The galvo system was calibrated by mapping angular deflections to lateral displacements at the sample plane using a standard grid pattern, ensuring minimal distortion over a $100\ \mu\text{m} \times 100\ \mu\text{m}$ writing area. The PEGDA-based photo-polymer thin film was mounted on a piezoelectric nanotranslation stage (Physik Instrumente, PI-545), providing sub-nanometer axial positioning for precise layer-by-layer volumetric encoding.

GS writing was controlled by custom software that converted 3D CAD models into synchronized galvo scanning commands. Laser pulse emission was temporally coordinated with galvo positions using a high-precision timing controller, while an acousto-optic modulator (AOM) served as an optical shutter for precise gating. This arrangement ensured that each voxel received a well-defined pulse dose at an accurate spatial location, preventing voxel overlap or spacing errors and enabling deterministic placement without lateral motion of the nanopiezo stage. Consequently, high-speed lateral writing was achieved while maintaining consistent u-CPDs formation and uniform UCPL emission across the encoded volume.

Wide-field readout beam configuration

For wide-field readout, an 808 nm CW laser (Coherent, OBIS LX, 150 mW) was collimated and directed onto a scanning micromirror (LBTEK, MEMS-1.3-1.15K, $\varnothing$ 1.3 mm). Operating at a resonance frequency of ~ 5.8 kHz with a minimum angular step of 0.05° and $\pm 30^\circ$ optical scanning range, the micromirror enabled rapid beam scanning and efficient spatial averaging. The scanned beam was relayed to the back-pupil plane of an oil-immersion high-NA objective (Olympus, UPlanApo 100 $\times$ /1.5 NA) via a focusing lens (JCOPTIX, OLC240166-T3M, $f = 200$ mm), creating an epi-illumination setup suitable for wide-field excitation (**Supplementary figs 2A, 2C, and 3B**).

UCPL emitted by the u-CPDs was collected by the same objective and spectrally separated from the excitation beam using a dichroic mirror (Semrock, Di03-R785-t3-25 $\times$ 36). The signal was imaged onto a high-sensitivity electron-multiplying CCD (EMCCD) camera (Andor, iXon Ultra 888; 1024×1024 pixels, $13\ \mu\text{m}$ pixel pitch, $>90\%$ quantum efficiency) through an imaging lens (JCOPTIX, OLC240136-T2M, $f = 50$ mm).

The EMCCD was operated in electron-multiplication mode and thermoelectrically cooled to $-60\ ^\circ\text{C}$ to suppress dark current and readout noise, enabling near single-photon sensitivity under low-signal UCPL conditions. A notch filter (LBTEK, ZET808NF) suppressed residual excitation light, while a short-pass filter (Semrock, BSP01-785R-25) isolated the UCPL emission band, minimizing background noise.

Performance and throughput

This GS writing and wide-field readout architecture enabled parallel readout of multiple voxels, substantially increasing data throughput compared to confocal point-scanning systems. The combination of non-mechanical lateral writing and wide-field UCPL imaging enhanced lateral writing speed while maintaining voxel size and UCPL intensity. This scalable platform is therefore well suited for large-area, high-density 3D optical disk fabrication, balancing spatial resolution, temporal efficiency, and photon collection efficiency.

1.3 Writing Time-Response Characterization System

The writing time-response characterization system (**Supplementary fig 4**) was implemented on a custom-built confocal microscopy platform, designed for precise control of ultrafast laser–matter interactions. Samples were mounted on a computer-controlled three-axis piezoelectric nanopositioning stage (Physik Instrumente, P-563.3CL), providing sub-nanometer spatial accuracy during laser exposure. Writing was performed using a 460 nm fs laser source (Light Conversion, ORPHEUS-HP) delivering pulses shorter than 205 fs, with a tunable repetition rate ranging from 100 Hz to 100 kHz. For time-response measurements, the repetition rate was fixed at 100 Hz to allow unambiguous control over the number of laser pulses per writing event.

The collimated beam was attenuated using a half-wave plate and polarizing beam splitter for precise pulse energy control, followed by a quarter-wave plate to generate circular polarization and ensure consistent excitation conditions. The beam was directed by a dichroic mirror and tightly focused onto the sample via an oil-immersion high-NA objective lens (Olympus, UPlanApo 100×/1.5 NA). Writing time was precisely regulated using an optical shutter (Thorlabs, SH1/M), enabling controlled exposure down to single-pulse delivery per shutter opening.

Temporal modulation of the writing process was achieved by varying the shutter opening duration and, when required, adjusting the laser repetition rate. This configuration allowed deterministic delivery of pulse sequences with defined inter-pulse intervals, ensuring that each writing event corresponded to an exact and known number of laser pulses. By systematically varying the pulse count, the temporal evolution of *in situ* photo-carbonization and u-CPDs formation was investigated, providing quantitative insight into writing kinetics, threshold behavior, and intensity modulation mechanisms governing u-CPDs generation.

The energy dose delivered to each voxel was calculated based on measured pulse energy and the number of incident pulses. At low pulse counts, a near-linear relationship between incident energy dose and UCPL intensity was observed, identifying the regime suitable for deterministic u-CPDs formation. By progressively decreasing the pulse count, the minimum writing time required for detectable u-CPDs generation was

determined, establishing the writing threshold and enabling precise voxel-level encoding with minimal energy input.

1.4 Readout Time-Response Characterization System

A readout time-response characterization system was implemented to probe the temporal evolution (lifetime) of UCPL under modulated excitation. The UCPL lifetime characterization system (**Supplementary fig 5**) used a waveform generator (RIGOL DG5072) to modulate the intensity of an 808 nm CW laser, generating a square wave pulse with a width of 100 μ s and a repetition frequency of 1 kHz. This modulation scheme mimics temporal dynamics relevant to practical readout operations. The modulated laser beam was focused onto the PEGDA photo-polymer film to excite *in situ* laser-written u-CPDs.

UCPL emission was collected and spectrally filtered using a short-pass filter (Semrock SP01-785RU-25) to suppress residual excitation light, followed by a band-pass filter (JCOPTIX OFBH110-730) to isolate the target emission band. The filtered signal was coupled into an optical fiber and directed to a time-correlated single-photon counting (TCSPC) module (Zolix, DCS900PC) for lifetime analysis.

Decay profiles were analyzed to extract the effective UCPL emission lifetime (τ_{eff}), which captures the combined effects of radiative recombination and phonon-assisted non-radiative relaxation processes. The observed decay curves provided direct evidence of phonon-assisted relaxation pathways in u-CPDs embedded within the PEGDA polymer matrix.

The effective lifetime τ_{eff} was calculated from the recorded decay curves according to:

$$\tau_{eff} = \frac{1}{I_0} \int_0^{\infty} I(t) dt \quad (1)$$

where $I(t)$ denotes the UCPL emission intensity recorded as a function of time t and I_0 is the maximum emission intensity.

1.5 Down-Conversion Fluorescence (DCF) Wide-Field Readout System

DCF imaging served as an auxiliary readout and validation technique, confirming successful laser patterning and providing an independent comparison with UCPL-based measurements. In particular, it enabled assessment of the influence of laser writing energy on emission efficiency and spatial uniformity without reliance on upconversion processes, offering complementary insight into the photophysical properties of the laser-modified polymer regions.

DCF imaging of the laser-fabricated patterns was performed using a commercial wide-field fluorescence microscope (Olympus, BX53) equipped with LED-based excitation

(**Supplementary fig 6**). The system featured interchangeable excitation modules covering UV (340–390 nm), blue (460–495 nm), and green (530–550 nm) spectral bands, enabling systematic characterization of DCF emission from PEGDA-based photo-polymer thin films under multiple excitation conditions. This multi-band excitation capability allowed evaluation of excitation-dependent spectral response and emission efficiency of DCF-active regions generated at different laser writing energies.

For routine wide-field inspection, a 20× objective lens (Olympus, UPlanXApo 20×/0.8 NA) was used, providing a large field of view suitable for assessing the spatial distribution, uniformity, and macroscopic morphology of the written emission patterns. LED illumination combined with spectrally matched filter cubes ensured stable and reproducible excitation conditions. Compared with UCPL readout, DCF imaging exhibited a higher background level due to residual autofluorescence of the PEGDA matrix; nevertheless, the use of narrow-band excitation and emission filters significantly improved image contrast, enabling reliable visualization of DCF patterns.

High-resolution DCF imaging was carried out using an oil-immersion high-NA objective (Olympus, UPlanApo 100×/1.5 NA). All measurements were performed in an epi-illumination configuration, with excitation delivered through the objective and DCF collected along the same optical path. Emission was detected using the microscope's high-sensitivity sCMOS camera in combination with appropriate bandpass emission filters (Semrock). Specifically, the DCF signals were isolated using a series of long-pass filters, including BA420IFS (430–700 nm), BA510IFS (517–700 nm), and BA575IFS (580–700 nm), corresponding to the UV, blue, and green excitation channels, respectively. This ensured efficient collection of down-converted photons while suppressing excitation leakage.

Both bright-field and fluorescence imaging modes were employed to correlate luminescent features with the underlying polymer morphology and to accurately locate laser-written structures within the focal plane using the microscope's fine-focus mechanism. For spectral characterization, DCF emission from selected regions was coupled through the microscope camera port into a fiber-coupled spectrometer, allowing quantitative analysis of excitation-dependent emission spectra under UV, blue, and green excitation.

The key experimental parameters for static and dynamic laser writing and readout systems are shown in **Table S1**.

Supplementary Note 2: Materials Synthesis and Device Fabrication

2.1 Synthesis of PEGDA-Based Photo-Polymer Thin Films

All reagents used for synthesizing and fabricating the PEGDA-based photo-polymer thin films were purchased from Sigma-Aldrich and used as received without further

purification. PEGDA ($M_n = 575$ Da) was selected as the photo-monomer and multifunctional cross-linker due to its excellent chemical stability, high optical transparency, and suitability for laser-based micro- and nanofabrication (**Supplementary fig 7**). PEGDA forms robust polymer networks through photopolymerization of its acrylate groups, enabling precise spatial and temporal control over polymerization under light irradiation. These properties make it well suited for high-resolution 3D laser writing and photonic applications requiring both mechanical robustness and optical clarity.

Diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) was used as the photo-initiator (PI). TPO is an acyl phosphine oxide initiator with strong absorption in the UV–visible spectral region below 420 nm and high radical generation efficiency in acrylate-based systems. Upon photoexcitation, TPO undergoes P–C bond cleavage, generating benzoyl and diphenylphosphinyl radicals that initiate polymerization by reacting with the C=C double bonds of PEGDA. Under high-intensity or prolonged irradiation, radical-mediated polymer fragmentation and partial carbonization may occur, promoting the formation of carbon-rich structures within the polymer matrix.

The PEGDA-based photo-polymer thin films were fabricated using a spin-coating technique. Briefly, a homogeneous PEGDA solution containing 4 wt% TPO was prepared and applied to a glass coverslip (Electron Microscopy Sciences, #0, 22 mm × 22 mm, thickness 0.08-0.1 mm) using a micro-pipette. The substrate was then spin-coated at 8,000 rpm for 20 s to achieve uniform film thickness, followed by thermal treatment on a hot plate at 80 °C for 30 min to promote uniform cross-linking and solvent evaporation before natural cooling to room temperature (**Supplementary fig 8A**). Subsequently, the coated films were cured to initiate photopolymerization and form solid photo-polymer thin films. This post-baking step yielded mechanically stable, optically homogeneous films suitable for *in situ* laser writing and readout. Step-height profilometry confirmed a thickness of ~280 μm (**Supplementary fig 8B**). Film thickness and lateral uniformity were reproducibly controlled by adjusting spin speed and solution volume, which is critical for consistent 3D laser writing.

2.2 Fabrication of a PEGDA-based Photo-Polymer Optical Disks

PEGDA-based photo-polymer optical disks were fabricated using a modified spin-coating technique optimized for large-area substrates. A PEGDA-based photo-polymer solution identical to that used for thin-film preparation was applied onto a transparent polymer disk base with a diameter of 12 cm and a thickness of 1.1 mm using a micro-pipette. To achieve uniform coverage across the entire disk surface, a three-step spin-coating process was employed: 300 rpm for 20 s, 1,000 rpm for 10 s, and 8,000 rpm for 20 s. This multi-step spin-coating strategy allowed the polymer solution to spread gradually, reduced thickness gradients, and eliminated excess solvent during the final high-speed step.

After coating, the disk was heated on a hot plate at 80 °C for 30 minutes and then allowed to cool naturally to room temperature. The post-baking process promoted solvent evaporation and film stabilization, resulting in optically transparent and mechanically robust photo-polymer layers.

This high degree of uniformity is essential for consistent laser writing and readout performance in large-area optical disk applications. The resulting photo-polymer layers exhibited high optical transparency throughout the visible spectrum and sufficient mechanical integrity to withstand handling and disk rotation during high-speed laser writing, as confirmed by visual inspection and gentle flexural testing.

Supplementary Note 3: Characterization Methods

3.1 Optical, Structural, and Spectroscopic Characterization

PEGDA-based photo-polymer thin films were characterized using a Leica optical microscope equipped with a high-precision light source and photodetector. Transmission measurements across the visible and near-infrared revealed high transparency and minimal scattering, indicating excellent optical clarity. Imaging under varied illumination confirmed uniformity and homogeneity, supporting their suitability for high-resolution laser writing and readout.

Luminescence emission spectroscopy was performed using an Avantes AvaSpec-ULS2048CL-EVO spectrometer. Excitation was provided by an 808 nm CW laser (Coherent, OBIS LX, 150 mW), enabling characterization of UCPL from laser-written regions.

Optical microscopy imaging was carried out using a Leica DM2700M microscope equipped with a Leica DFC295 digital color camera, enabling high-resolution visualization of surface morphology and laser-written patterns. Film thickness and surface step-height measurements were obtained using a DektakXT stylus profilometer to assess coating uniformity and structural fidelity of the photo-polymer films.

UV–visible absorption spectroscopy was performed with a UV-2600i UV-visible spectrophotometer to evaluate optical absorption characteristics of the PEGDA-based photo-polymer thin films, without and with TPO, showed strong absorption below 420 nm, enabling effective photopolymerization under 460 nm fs laser irradiation via two-photon excitation (**Supplementary fig 9**).

Fourier transform infrared (FTIR) spectroscopy was conducted using a Thermo Fisher Nicolet iS20 to investigate polymer cross-linking and chemical structure. FTIR spectroscopy performed before and after thermal treatment confirmed successful cross-linking of PEGDA. The reduction of the characteristic acrylate C=C stretching band at 1635 cm⁻¹ indicated effective polymerization, while the C=O stretching (1720 cm⁻¹)

and C–O asymmetric stretching (1194 cm^{-1}) bands remained largely unchanged, confirming preservation of the PEGDA backbone (**Supplementary fig 10**). These results demonstrate that the fabrication process yields mechanically stable, optically homogeneous films suitable for reproducible 3D laser writing and u-CPDs generation.

3.2 Thermal Properties and Stability

Thermal properties and stability were evaluated using thermogravimetric analysis (TGA) and derivative thermo gravimetry (DTG) on a TA Instruments Q5000 system. TGA curves showed minimal mass loss at moderate temperatures, indicating high thermal stability under fs laser writing and CW readout conditions. Significant mass loss occurred only at elevated temperatures, confirming the structural integrity of the films during laser-induced photo-carbonization.

TGA and DTG measurements (**Supplementary fig 11**) reveal excellent thermal robustness of the PEGDA matrix. The polymer exhibits negligible mass loss up to approximately $346\text{ }^{\circ}\text{C}$, indicating that the cross-linked network remains structurally stable over a wide temperature range. Rapid weight loss occurs between $\sim 350\text{ }^{\circ}\text{C}$ and $\sim 410\text{ }^{\circ}\text{C}$, corresponding to thermal decomposition of the PEGDA backbone and scission of acrylate-linked PEG chains. The maximum degradation rate occurs at $\sim 378\text{--}381\text{ }^{\circ}\text{C}$ for both PEGDA-based photo-polymer thin films without and with PI, indicating that PI incorporation does not significantly alter intrinsic thermal stability.

Differential scanning calorimetry (DSC) was performed with a TA Instruments DSC2500 system. The DSC thermograms revealed no low-temperature phase transitions, indicating that the polymer matrix remains stable even at sub-ambient temperatures. The consistent thermal response demonstrates the robustness of the PEGDA films, ensuring material integrity during fabrication, fs-laser processing, and operational use in optical devices.

DSC measurements (**Supplementary fig 12**) further confirm the thermal robustness. The PEGDA-based photo-polymer thin films without PI exhibits a pronounced endothermic transition with a peak temperature of $\sim 156.8\text{ }^{\circ}\text{C}$ and onset at $\sim 124.3\text{ }^{\circ}\text{C}$, attributed to thermal relaxation and segmental rearrangement within the cross-linked polymer network. With PI, the transition peak shifts slightly to $\sim 152.2\text{ }^{\circ}\text{C}$, with a modest reduction in enthalpy, suggesting minor structural modifications while preserving overall thermal behavior.

3.3 Photophysical Response and Laser-Induced Effects

The TPO concentration was optimized to balance photopolymerization efficiency, optical transparency, and the formation of carbon-rich u-CPDs. TPO concentrations below 4% resulted in incomplete cross-linking, while higher concentrations increased optical absorption, leading to excessive carbonization and reduced film transparency.

The UCPL response of PEGDA-based photo-polymer thin films, both without and with the PI, was evaluated under 808 nm CW laser irradiation following exposure to a 460 nm fs laser at various power levels (**Supplementary fig 13**).

Threshold behavior and morphological changes associated with increasing irradiation energy were investigated through single-pulse u-CPDs formation at varying fs-laser power levels (**Supplementary fig 14**). These results confirm the transition from localized photo-polymerization to carbonization.

The influence of pulse accumulation on nanoscale carbonization is illustrated by confocal UCPL and bright-field images of u-CPDs generated with varying pulse numbers at a constant laser power of 0.15 μ W (**Supplementary fig 15**).

3.4 Optical Data Encoding and Pattern Characterization

Systematic characterization of optical data bit patterns was conducted via confocal microscopy by detecting UCPL under 808 nm CW laser irradiation (1 mW power, 5 ms pixel dwell time). Patterns were fabricated using a 460 nm fs laser at power levels of 10–30.5 mW with a fixed exposure time of 10 ms, yielding UCPL images and intensity profiles that demonstrate a direct correlation between writing power and signal intensity (**Supplementary fig 16**).

Investigation of exposure times ranging from 90 ms to 2,000 ms at a fixed power of 10 mW confirms temporal control over the luminescence contrast of the recorded bits (**Supplementary fig 17**). The relationship between UCPL signals and the total energy dose (0.1 mJ to 20.5 mJ) was further established through confocal imaging and intensity profile analysis, defining the operational range for reliable data encoding (**Supplementary fig 18**).

3.5 Advanced Chemical and Structural Analysis

Localized optical absorption properties of laser-written regions were further examined by micro-absorption spectroscopy using a BX53M microscope system (**Supplementary fig 19**). Bulk and spatially resolved absorption measurements were used to assess optical uniformity and to verify that laser processing did not introduce undesirable absorption variations across the film.

Micro-Raman spectroscopy was conducted with an Andor Shamrock 500i imaging spectrometer, excited by a 532 nm CW laser (Laser Quantum Torus). The excitation power was varied to accommodate different measurement conditions and to probe laser-induced structural changes and carbonization behavior. Raman spectroscopy provided complementary information on carbon-rich structures and structural modifications induced by fs laser processing (**Supplementary fig 20**).

The micro-FTIR measurements were carried out using a Thermo Fisher iN10 system, achieving spatial resolution for chemical analysis, thereby enabling the assessment of the chemical consistency between the laser-written area and the unmodified area (**Supplementary fig 21**).

Elemental composition and chemical state analysis were performed using micro-X-ray photoelectron spectroscopy (XPS) with a Shimadzu AXIS Supra+ instrument equipped with a monochromatic Al K α X-ray source (1486.68 eV). XPS confirmed the formation of carbon-rich structures, the presence of oxygen-containing functional groups, and successful incorporation of photochemically generated u-CPDs within the PEGDA polymer matrix (**Supplementary figs 22 and 23, and Table S2**).

3.6 UCPL Lifetime Stability and Measurement Conditions

The UCPL lifetime measurements remained nearly constant at $\sim 1.72 \mu\text{s}$ over 14 repeated measurement cycles (**Supplementary fig 24 and Table S3**), with variations limited to $\sim 1.4\text{--}2.1 \mu\text{s}$ ($\sim 5\%$ relative fluctuation) and no systematic drift. This demonstrates that the PEGDA-based photo-polymer matrix effectively stabilizes localized electronic states and that the u-CPDs maintain well-defined excited-state dynamics.

All material characterizations were performed at room temperature unless otherwise specified.

Supplementary Note 4: Formation Mechanism of *In Situ* Written u-CPDs

We propose a model for the formation of *in situ* laser-written u-CPDs in a PEGDA-based photo-polymer, addressing two scenarios: PEGDA without TPO and PEGDA with TPO. The formation of u-CPDs under the irradiation of a 460 nm fs laser involves two primary mechanisms [1–3]: photo-cross-linking of polymer clusters and photo-carbonization (**Supplementary fig 25**). These processes result in the formation of UCPL-emissive functional groups within the PEGDA-based photo-polymer. The observed UCPL is attributed to the creation of carbon-rich graphitic domains within the u-CPDs and the presence of UCPL-emissive functional groups, such as carbonyl (C=O) groups.

For characterizing the formed u-CPDs, we focus on detecting phonon-assisted UCPL in the PEGDA-based photo-polymer under the irradiation of an 808 nm CW laser. We highlight the interplay between laser-induced chemical transformations and the resulting optical properties of the material. Specifically, we propose that the intensity of UCPL from the PEGDA-based photo-polymer I_{UCPL} , when irradiated with an 808 nm CW laser, is directly proportional to the quantity of u-CPDs N_{u-CPDs} containing UCPL-emissive functional groups formed during irradiation with the 460 nm fs laser, according to:

$$I_{UCPL} \propto N_{u-CPDs} \quad (2)$$

The formation of u-CPDs and the resulting phonon-assisted UCPL from the PEGDA-based photo-polymer proceed through distinct phases that closely resemble the S-shaped curve of a logistic function. These phases arise from the complex interplay between chemical kinetics, light-induced reactions, and physical constraints. The logistic function offers a clear framework to model these reaction dynamics, dividing them into three stages:

1. *Lag Phase:* In the initial stage, light triggers the decomposition of molecules, producing free radicals. These radicals then interact with PEGDA monomers, initiating the processes of photo-cross-linking and photo-carbonization. However, the reaction rate remains slow at this point due to the gradual accumulation of active radicals and the homogeneous distribution of monomers, leading to minimal photo-cross-linking and photo-carbonization. As a result, the increase in phonon-assisted UCPL during this phase is modest. In the case of PEGDA combined with TPO, this lag phase is considerably shortened. Furthermore, the lower activation threshold of TPO facilitates faster radical generation, accelerating the onset of photo-cross-linking and photo-carbonization processes.
2. *Exponential Growth Phase:* As the reaction progresses, the concentration of radicals rises sharply, which accelerates the processes of photo-cross-linking and photo-carbonization. During this phase, there is an abundant supply of monomers, stronger interactions between radicals and monomers, and rapid accumulation of u-CPDs. These factors collectively lead to a significant increase in phonon-assisted UCPL. In the PEGDA + TPO system, this phase is triggered with a lower threshold and progresses more quickly compared to direct PEGDA, owing to the enhanced efficiency provided by the PI.
3. *Plateau Phase:* As the reaction nears completion, the rate of photo-cross-linking and photo-carbonization slow and eventually stabilize at its maximum. This deceleration is due to the depletion of monomer concentrations and the increasing density of photo-carbonized species, which hinders the diffusion of radicals and monomers. Additionally, termination processes, such as radical recombination or limitations imposed by the light source, become more prominent. In the PEGDA + TPO system, the plateau phase is reached sooner and results in higher intensity of phonon-assisted UCPL, reflecting the faster reaction kinetics and lower energy threshold for the process.

These three phases effectively capture the reaction dynamics of photo-cross-linking and photo-carbonization, with the logistic curve offering a robust model for understanding the complex interplay between chemical transformations and the resulting phonon-assisted UCPL, expressed by:

$$N_{u-CPDs} = \frac{K}{1 + e^{-r(t-t_0)}} \quad (3)$$

where N_{u-CPDs} is the concentration of u-CPDs at time t , K is the maximum concentration that can be reached (the carrying capacity), r is the growth rate, and t_0 is the inflection point (the time at which the growth rate is highest). The extent of photo-cross-linking in polymer clusters and photo-carbonization is influenced by factors such as light intensity, photo-monomer and PI concentration, and exposure time. The logistic function effectively captures the interaction between these variables, offering a straightforward yet powerful framework for modeling the formation of *in situ* laser-written u-CPDs in a PEGDA-based photo-polymer.

Supplementary Note 5: Modeling of Phonon-Assisted UCPL

Phonon-assisted UCPL (**Supplementary fig 26**) is a process where low-energy photons are converted into higher-energy emitted photons with the help of phonons, which are quantized lattice vibrations within a material. Unlike conventional upconversion mechanisms, such as multi-photon absorption or energy transfer, phonon-assisted UCPL relies on the interaction between electronic states and vibrational energy levels facilitated by phonons.

In the case of phonon-assisted UCPL from *in situ* laser-written u-CPDs in a PEGDA-based photo-polymer, localized electronic states within the material are key to the process. These states arise from structural defects and functional groups, such as sp^3 hybrid defects and oxygen functional groups in graphitic domains under 460 nm fs laser irradiation [2,3]. These localized states provide intermediate energy levels that interact with lattice vibrations, increasing the probability of phonon-mediated transitions.

Under irradiation with an 808 nm CW laser, the material absorbs low-energy photons, which elevate electrons to intermediate or excited electronic states. In phonon-assisted UCPL, phonons bridge the energy gap between these electronic states, allowing the electron to reach a higher energy level. The electron then undergoes radiative recombination, emitting a photon of higher energy (shorter wavelength) than the initially absorbed photon.

The phonon population N_P of a specific mode obeys Bose-Einstein statistics, as:

$$N_P = \frac{1}{e^{E_P/k_B T} - 1} \quad (4)$$

where E_P is the phonon energy, k_B is the Boltzmann constant and T is temperature. The probability of the electronic transition coupling simultaneously with n phonons is proportional to the n -th power of the phonon population.

$$P \propto (N_P)^n = \left(\frac{1}{e^{E_P/k_B T} - 1} \right)^n \quad (5)$$

Equations (5) and (6) provide a quantitative framework for predicting phonon-assisted UCPL intensity based on phonon population and the number of phonons involved in electronic transitions. Phonon-assisted UCPL depends on the phonon population, which follows Bose-Einstein statistics. Increasing temperature excites more phonons, enhancing the probability of phonon-mediated electronic transitions and increasing UCPL intensity (**Supplementary fig 27**). Consequently, UCPL intensity increases with temperature, as a higher phonon population facilitates more frequent phonon-mediated electronic transitions.

This relationship allows us to calculate UCPL intensity by considering interactions between the phonon population and energy gap between electronic states, with more phonons enhancing phonon-mediated transitions and boosting UCPL intensity. Understanding this mechanism allows us to optimize material design and laser parameters to maximize phonon-assisted UCPL, which is crucial for applications in high-density optical storage and photonic devices.

Supplementary Note 6: Optical Data Encoding Strategies

6.1 Bit-Wise and Image-Wise Encoding Strategies

A novel optical data encoding workflow is illustrated in **Supplementary fig 28**. Compared to conventional bitwise multilevel encoding (standard 8 bits/pixel), this approach enables an encoding density of up to 10 bits/pixel. At the conceptual level, two encoding paradigms are defined: *bit-wise encoding*, where individual optical data bits are written and read in a serial, pixel-by-pixel manner with discrete intensity levels, and *image-wise encoding*, where entire spatial patterns are encoded and retrieved in parallel using distributed intensity modulation.

In bit-wise encoding, the data capacity is limited by the number of distinguishable intensity levels per pixel, typically constrained by signal-to-noise and readout limitations. In contrast, image-wise encoding leverages spatial correlations, parallel detection, and global intensity variations across the pattern, enabling more efficient use of the available dynamic range. This allows additional encoding degrees of freedom beyond single-pixel intensity, effectively increasing the achievable encoding density.

These strategies are implemented through two complementary system configurations: static confocal writing and readout, which provides precise control at the single-bit level, and GS-assisted dynamic writing combined with wide-field readout, which enables high-throughput, large-area parallel processing.

6.2 Confocal *In Situ* Writing and Readout

In the confocal configuration, both writing and readout are performed in a static, point-by-point manner, enabling precise control of individual optical data bits.

High-resolution microstructural fabrication was achieved via localized photo-carbonization induced by a 460 nm fs laser (10 mW) in PEGDA-based photo-polymer thin films. By modulating exposure times (10–2200 ms), complex optical patterns with varying contrast were fabricated, as confirmed by bright-field optical microscopy images (**Supplementary fig 29**). The precision of this localized process was further validated through the creation of “running cat” patterns using confocal *in situ* writing (**Supplementary fig 30**), which serve as sequential frames for 3D HD movie encoding.

6.3 GS-Assisted Writing and Wide-Field Readout

To enable large-area data recording, a GS-assisted dynamic scanning system was introduced. This approach combines dynamic writing with parallel wide-field readout, providing significant advantages in throughput and scalability compared to static confocal operation.

At the bit level, controlled modulation of luminescence intensity was achieved by varying exposure conditions, as confirmed by wide-field UCPL images and corresponding line intensity profiles, which show high spatial contrast between recorded data bits (**Supplementary fig 31**).

The GS-assisted system enabled continuous large-area patterning, successfully generating extended structures (**Supplementary fig 32**). These patterns were efficiently read out using wide-field UCPL detection with different microscope objectives (40× and 100×), demonstrating high-throughput parallel imaging capability (**Supplementary fig 33**). The high spatial precision of the localized process was further confirmed by fabricating “running cat” patterns via GS-assisted scanning (**Supplementary fig 34**), which serve as sequential frames for 3D HD movie encoding.

6.4 Wide-Field DCF and Imaging

Spectroscopic measurements indicate that DCF exhibits excitation-dependent fluorescence under UV, blue, and green illumination (**Supplementary fig 35**), enabling its use as an alternative readout mechanism. In this approach, optical patterns are recorded via confocal writing and read out through wide-field detection of DCF fluorescence.

Clear fluorescence patterns were obtained under 100× objectives (**Supplementary fig 36**), demonstrating that DCF-based readout effectively resolves recorded structures across different spatial scales and serves as a complementary strategy for optical data

recording and parallel imaging.

Supplementary Note 7: Storage Capacity Calculation

The storage capacity of the PEGDA-based photo-polymer optical disk is calculated based on the number of gray levels (intensity levels) N , the size of the storage medium, and the resolution of the optical system. In our system, the number of distinguishable intensity levels (signal-to-noise ratio-based gray levels, N) is determined by the dynamic range of UCPL emitted by the laser-written u-CPDs. The dynamic range is quantified as the ratio between the maximum UCPL signal and the minimum detectable signal above background noise. In our optical disk:

$$N = \frac{I_{max} - I_{min}}{I_{background}} \quad (6)$$

where I_{max} represents the maximum number of emitted photons by u-CPDs, I_{min} represents the minimum number of emitted photons, and $I_{background}$ represents the background noise signal. In our experiment, $I_{max} = 5,500,000$, $I_{min} = 6,000$, and $I_{background} = 2,000$, yielding a calculated N value of approximately 2,700. This directly determines the number of bits that can be stored per voxel, linking the photophysical properties of the u-CPDs to the overall disk storage capacity.

Theoretically, the maximum number of bits that can be encoded in one voxel is determined by N , so the information per voxel (in bits) is $\log_2(N) = 11$ bits. Our HD optical disk encoding experimentally achieves 10 bits, that is 2^{10} intensity levels, which corresponds to 1,024 grayscale levels. With bit spacing set to 1 μm and layer spacing to 5 μm , and considering the ability to record in the volume of the optical disk, the theoretical maximum storage capacity of the optical disk is estimated at 400 terabits (Tb) within a DVD-sized optical disk.

The lateral bit spacing and vertical layer spacing determine the achievable voxel density, allowing for the integration of hundreds of densely packed layers within a single DVD-sized disk. By fully utilizing the polymer's volume, this 3D encoding strategy significantly enhances storage capacity, overcoming the limitations of traditional 2D planar disks.

Supplementary Note 8: Bit Error Rate (BER) Analysis

The error rate of the PEGDA-based optical disk is quantified using the BER, which measures the frequency of errors during data readout. BER is defined as the ratio of erroneous bits E to the total number of bits read N :

$$BER = \frac{E}{N} \quad (7)$$

To determine BER experimentally, multiple regions of the PEGDA-based optical disk were read under controlled laser excitation, ensuring consistent focus, power, and scanning speed to mimic practical readout conditions. The distribution of readout errors was analyzed statistically, confirming that errors occurred randomly and were not clustered, which is essential for reliable decoding and robust data retrieval.

In our experiments, fewer than 5 erroneous bits were detected for every 100,000 bits read, corresponding to a BER of approximately 10^{-5} . This translates to a readout reliability exceeding 99.99%, demonstrating the high fidelity achievable with volumetric multilevel encoding.

To ensure statistical confidence, each readout experiment was repeated across multiple independent cycles, covering different regions of the disk. This repetitive readout confirms that the observed low error rate is consistent and not due to localized anomalies or random fluctuations.

The low BER ($<10^{-5}$) under controlled laboratory conditions indicates that the system can reliably encode and retrieve data over many read cycles without significant degradation, which is critical for archival storage applications. Moreover, the high readout fidelity supports the use of high-density volumetric encoding, where multilevel grayscale and multilayer architectures require precise bit-level accuracy to fully exploit the volumetric storage potential.

Supplementary Note 9: Analysis of Writing and Readout Architectures

To evaluate the performance limits of the proposed 3D ODS platform, we estimate the achievable throughput of both the writing and readout subsystems. The analysis provides theoretical upper bounds as well as realistic performance estimates based on the parameters of the implemented optical system.

Writing Throughput

The achievable writing throughput is primarily determined by the repetition rate of the fs laser and the number of pulses required to generate a stable voxel through photo-carbonization of the PEGDA-based photo-polymer matrix. The writing laser operates at a repetition rate of $f_{rep} = 80$ MHz. If N_p pulses are required to generate a single voxel, the pulse-limited voxel generation rate is $R_{write} = f_{rep} / N_p$.

In the ideal case where a voxel is formed by a single pulse ($N_p = 1$), the theoretical upper bound becomes $R_{write,max} = 8.0 \times 10^7$ voxels s^{-1} , which corresponds to a binary writing throughput of $T_{write,max} = 80$ Mbit s^{-1} . In practice, multiple pulses are typically required to ensure reproducible voxel formation and stable UCPL emission.

If multilevel encoding is employed with b bits stored per voxel, the information

throughput becomes $T_{write} = b R_{write}$. For example, assuming a single pulse is used to generate a stable voxel and $b = 10$ bits are stored per voxel, the theoretical information throughput approaches $T_{write} \approx 800 \text{ Mbit s}^{-1}$.

A second constraint arises from the lateral scanning speed of the galvo mirrors. For the calibrated writing field of $100 \mu\text{m} \times 100 \mu\text{m}$ and a voxel pitch of $p = 300 \text{ nm}$, the number of voxel sites per layer is approximately $N_{layer} \approx 1.1 \times 10^5$, which follows from $N_{layer} \approx (100 \mu\text{m} / p)^2$.

During raster scanning, the number of scan lines required to cover the field is $N_{lines} \approx 100 \mu\text{m} / p \approx 333$. If scanning is performed with a line rate f_{line} , the time required to write a single layer becomes $t_{layer} = N_{lines} / f_{line} \approx 333 / f_{line}$. For representative galvo line rates of 1–10 kHz, the layer writing time therefore ranges from approximately 0.33 s to 0.033 s.

Under these conditions, the corresponding practical voxel writing rate is $R_{write,ach} = N_{layer} / t_{layer} \approx 3 \times 10^5 - 3 \times 10^6 \text{ voxels s}^{-1}$, which corresponds to an achievable binary throughput of approximately 0.3–3 Mbit s^{-1} , or 3–30 Mbit s^{-1} for 10 bits multilevel encoding.

Readout Throughput

Readout is performed using wide-field UCPL imaging on an EMCCD detector with 1024×1024 pixels. Because wide-field detection records many voxels simultaneously, the readout throughput is primarily determined by the frame rate rather than the dwell time per voxel.

Assuming a representative voxel pitch of 300 nm, the same $100 \mu\text{m} \times 100 \mu\text{m}$ field of view contains approximately $N_{layer} \approx 1.1 \times 10^5$ voxel sites. If each frame records the entire field, the information throughput can be expressed as $T_{read} = b N_{layer} f_{frame}$, where f_{frame} is the effective detector frame rate and b is the number of bits stored per voxel.

Assuming an exposure time of 1 μs , the theoretical detector-limited throughput becomes approximately $T_{read} \approx 1.1 \times 10^{11} \text{ bit s}^{-1}$ ($\approx 110 \text{ Gbit s}^{-1}$). For 10-bit multilevel encoding, the information throughput increases to approximately $T_{read} \approx 1.1 \times 10^{12} \text{ bit s}^{-1}$ ($\approx 1100 \text{ Gbit s}^{-1}$).

In practice, the achievable throughput is lower due to detector readout time and signal-to-noise requirements. For typical EMCCD frame rates of 20–100 fps, the practical binary readout throughput becomes 2–11 Mbit s^{-1} , or 20–110 Mbit s^{-1} for 10-bit multilevel decoding. Importantly, wide-field readout intrinsically benefits from spatial parallelism, allowing many voxel states to be decoded simultaneously.

Limitations and Practical Considerations

Several factors constrain the achievable throughput in the present configuration, although the architecture also provides several advantages compared with conventional optical disk technologies.

First, the voxel pitch assumed in the calculations (300 nm) directly determines the spatial sampling density and therefore the achievable throughput. Larger pitches reduce the effective storage density and throughput, whereas smaller pitches increase optical cross-talk and impose stricter focusing requirements. Nevertheless, the achievable pitch already approaches the diffraction-limited scale for near-infrared excitation and is comparable to the bit spacing used in state-of-the-art optical storage technologies such as Blu-ray disks. Furthermore, the use of 3D volumetric recording significantly increases the effective storage density compared with conventional planar optical disks.

Second, voxel formation in the PEGDA/u-CPDs system involves complex photochemical and thermal processes. The number of pulses required to generate a stable UCPL emitter may vary with local environment, laser intensity, and thermal accumulation. Variations in this pulse budget directly affect writing rates. However, this nonlinear photo-carbonization mechanism also enables highly localized voxel formation and stable luminescent contrast, which are advantageous for high-density 3D recording and multilevel encoding.

Third, the practical writing speed in the system is limited by galvo mirror acceleration, synchronization latency, and the gating precision of the AOM. These factors introduce overhead that reduces the effective voxel generation rate relative to the pulse-limited theoretical maximum. Despite these limitations, the scanning-based writing architecture is compatible with well-established laser processing technologies and could be further improved using faster beam steering systems, such as resonant scanners or acousto-optic deflectors, as demonstrated in high-speed laser fabrication platforms.

Fourth, readout throughput depends strongly on photon statistics. Reliable multilevel decoding requires sufficient photon counts to overcome shot noise, detector noise, and background luminescence. At the same time, the wide-field UCPL readout scheme offers an intrinsic advantage over conventional optical disk readout, which typically relies on sequential point scanning. By detecting large numbers of voxels simultaneously, wide-field imaging enables spatially parallel decoding and therefore provides a pathway toward substantially higher readout throughput.

Fifth, the present analysis assumes a single optical channel. Parallelization using multiple excitation beams or multiple storage tracks could proportionally increase the aggregate throughput, provided that optical cross-talk, laser power distribution, and detector dynamic range remain manageable. Such parallelization strategies are actively explored in next-generation optical storage systems and could be naturally integrated

with the present 3D recording architecture.

Supplementary Note 10: Operational Stability of u-CPDs

Comprehensive operational stability characterizations were performed to evaluate the performance and reliability of u-CPDs embedded in PEGDA-based photo-polymer thin films.

10.1 Writing Stability

Writing stability was evaluated on PEGDA-based photo-polymer thin films using a 460 nm fs laser across multiple pulse energy levels (0.2, 2, 5, 10, 15, and 20 mJ), covering a broad operational window for high-density data encoding. At each energy, 300 optical data bits were written using a computer-controlled positioning stage to ensure precise and repeatable laser focus placement (**Supplementary fig 37**). Statistical analysis of the UCPL intensity distributions showed that signal levels remained stable within ~8–12% of the mean with no systematic decay or drift, indicating a robust writing window for high-fidelity 3D data encoding.

10.2 Readout Stability and Cyclability

Long-Term Readout Stability

Long-term readout stability was evaluated on test patterns written at 10 mW with a 10 ms exposure time, subjected to continuous excitation using an 808 nm CW laser (1 mW) within a confocal microscopy configuration to ensure precise focusing and consistent detection. Continuous readout measurements (**Supplementary fig 38**) demonstrate that UCPL intensity remains stable over 30 min of excitation, with fluctuations limited to ~3–5% for writing energies between 5–20 mJ, where higher energies yield stronger emission due to more efficient formation of luminescent centers.

Long-term stability was further confirmed over 12 h of continuous excitation (**Supplementary fig 39**), with normalized UCPL intensity remaining within 0.96–1.04 (~8% variation) and no evidence of photobleaching. This sustained UCPL emission under prolonged readout conditions demonstrates the robustness of the PEGDA-based material and its suitability for reliable, long-term optical data retention and retrieval.

Readout Cyclability

Readout cyclability was evaluated by modulating the 808 nm CW laser (1 mW) between “ON” and “OFF” states using a shutter-controlled sequence at a fixed recorded location, consisting of 0.5 s illumination followed by 0.5 s of darkness for 50 consecutive cycles. Results from these repeated ON/OFF readout cycles (**Supplementary fig 40**) demonstrate stable luminescence throughout the cycling

process, with peak intensity fluctuations limited to ~6–7%.

UCPL intensity was continuously monitored during cycling. The emission remained stable across all cycles, indicating negligible photobleaching and confirming the high readout durability of the PEGDA-based photo-polymer thin films under repeated operation.

10.3 Accelerated Thermal Aging

To evaluate the durability and data retention capability of room-temperature encoding in PEGDA-based photo-polymer thin films, an accelerated thermal aging study was performed. Accelerated aging is a widely adopted methodology in ODS research, as it allows quantitative lifetime prediction by promoting thermally activated degradation processes within experimentally accessible timescales. In this study, PEGDA-based samples containing predefined 100×100 -bit arrays were subjected to controlled thermal stress to simulate extended operational aging under ambient storage conditions.

Thermal aging experiments were carried out by heating samples at 50, 75, 100, 125, and 150 °C for 1 h at each temperature in a vacuum drying oven (JINGHONG, DZF-6020TG). The vacuum environment minimized oxidative effects, isolating thermally driven degradation mechanisms intrinsic to the photo-polymer matrix and laser-written features. After each heat treatment, the UCPL intensity of the recorded bits was measured to assess the thermal stability of the encoded information.

The data lifetime, L , at each temperature was defined as the time required for the UCPL intensity to decay to 50% of its initial value, a commonly used criterion for functional data loss in optical storage systems. The temperature dependence of the extracted lifetimes was analyzed using the Arrhenius model, which describes thermally activated degradation kinetics. In its linearized form, the Arrhenius equation is expressed as:

$$L = Ae^{\frac{E_a}{RT}} \quad (8)$$

where E_a is the activation energy associated with the dominant degradation process, R is the gas constant, T is the absolute temperature, and A is the pre-exponential factor related to the intrinsic reaction rate. By fitting the experimentally determined lifetimes at elevated temperatures to the Arrhenius model, the degradation kinetics governing the stability of laser-generated u-CPDs within the PEGDA matrix were quantitatively characterized.

The resulting Arrhenius plot exhibited a clear linear relationship, indicating that the dominant degradation pathway follows a thermally activated process. Extrapolation of the fitted model to room temperature (300 K) yielded a median projected data lifetime under ambient conditions, the projected data retention lifetime at room temperature is ~43 years (**Supplementary fig 41**). Temperature-dependent measurements show that

UCPL emission remains stable below $\sim 90^{\circ}\text{C}$, while thermally activated quenching occurs above $\sim 100^{\circ}\text{C}$ (**Supplementary fig 42**).

The projected lifetime highlights the thermal robustness of the PEGDA-based photo-polymer matrix and the stability of the laser-generated u-CPDs. The accelerated aging results demonstrate that the PEGDA-based ODS platform combines efficient room-temperature data encoding with resistance to thermally induced degradation, satisfying key requirements for long-term data retention.

Supplementary Note 11: Implementation Perspective on PEGDA-Based u-CPDs Optical Disks in Optical Disk Drives

PEGDA-based photo-polymer thin films with *in situ* laser-written u-CPDs are compatible with standard optical disk drive form factors, enabling integration into commercial hardware. The disks maintain a 12 cm diameter and 1.2 mm thickness, matching DVD specifications, while spin-coated films provide uniform thickness and smooth surfaces, minimizing optical aberrations and maintaining consistent laser focus during read/write operations. The transparent PEGDA matrix supports 460 nm fs-laser writing and 808 nm CW readout with minimal scattering or absorption, allowing straightforward handling within conventional optical disk drives.

Practical 3D volumetric addressing requires synchronized high-precision galvo scanners or translation stages to achieve sub-diffraction voxel accuracy. Low-power readout lasers reduce the risk of thermal degradation of u-CPDs, while sensitive detectors such as SPADs enable high-fidelity UCPL signal acquisition. Multi-level encoding of up to 1,024 grayscale levels per voxel, together with low BER ($<10^{-5}$), allows precise data retrieval. Thermal stability of the polymer and disk flatness are critical to prevent interlayer crosstalk at micron-scale spacing, supporting repeatable volumetric storage.

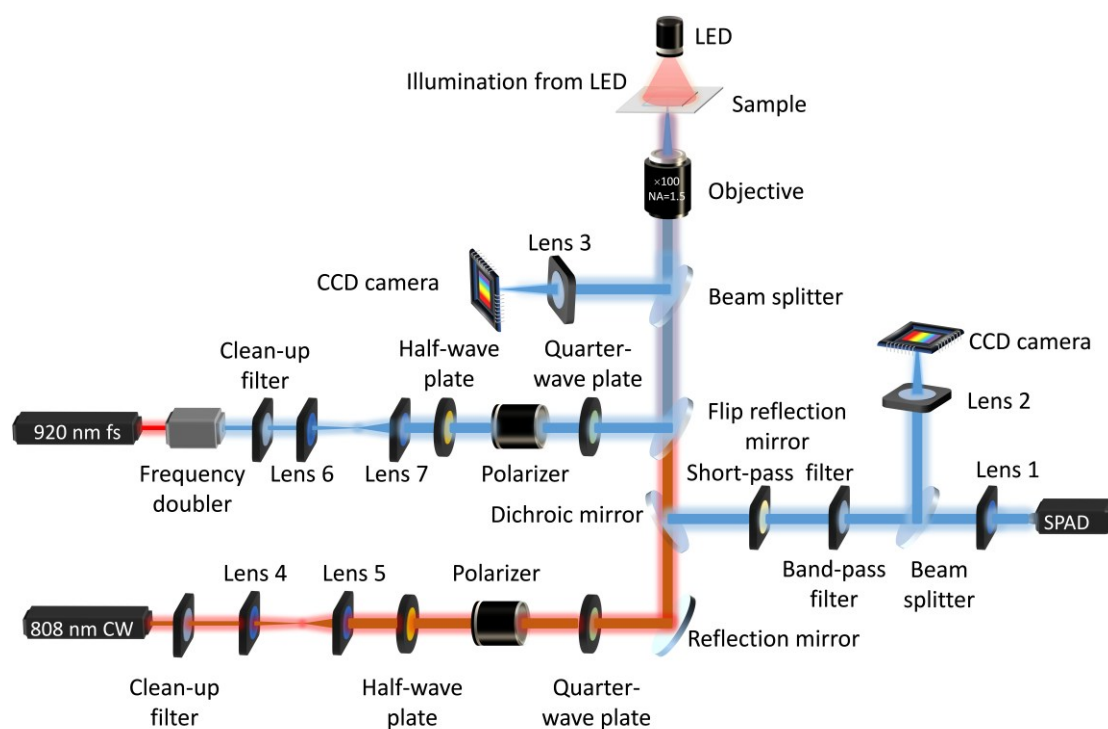
Parallelization strategies, including multi-beam GS writing and wide-field readout, can increase throughput, while multi-wavelength excitation and spectral multiplexing may provide additional opportunities to enhance volumetric data density. Optimization of polymer formulations, laser parameters, and voxel packing could enable storage capacities on the order of hundreds of terabits per DVD-sized disk with high reliability. Integration of adaptive optics, high-speed detectors, and standard disk packaging can further improve robustness and maintain compatibility with existing optical disk drives, helping bridge laboratory demonstrations and practical implementations.

From an implementation perspective, control software must support 3D addressing, layer selection, and error correction, while maintaining grayscale fidelity and low bit errors. The combination of low-power readout and the thermal stability of PEGDA mitigates inadvertent u-CPDs alteration, supporting operational reliability over

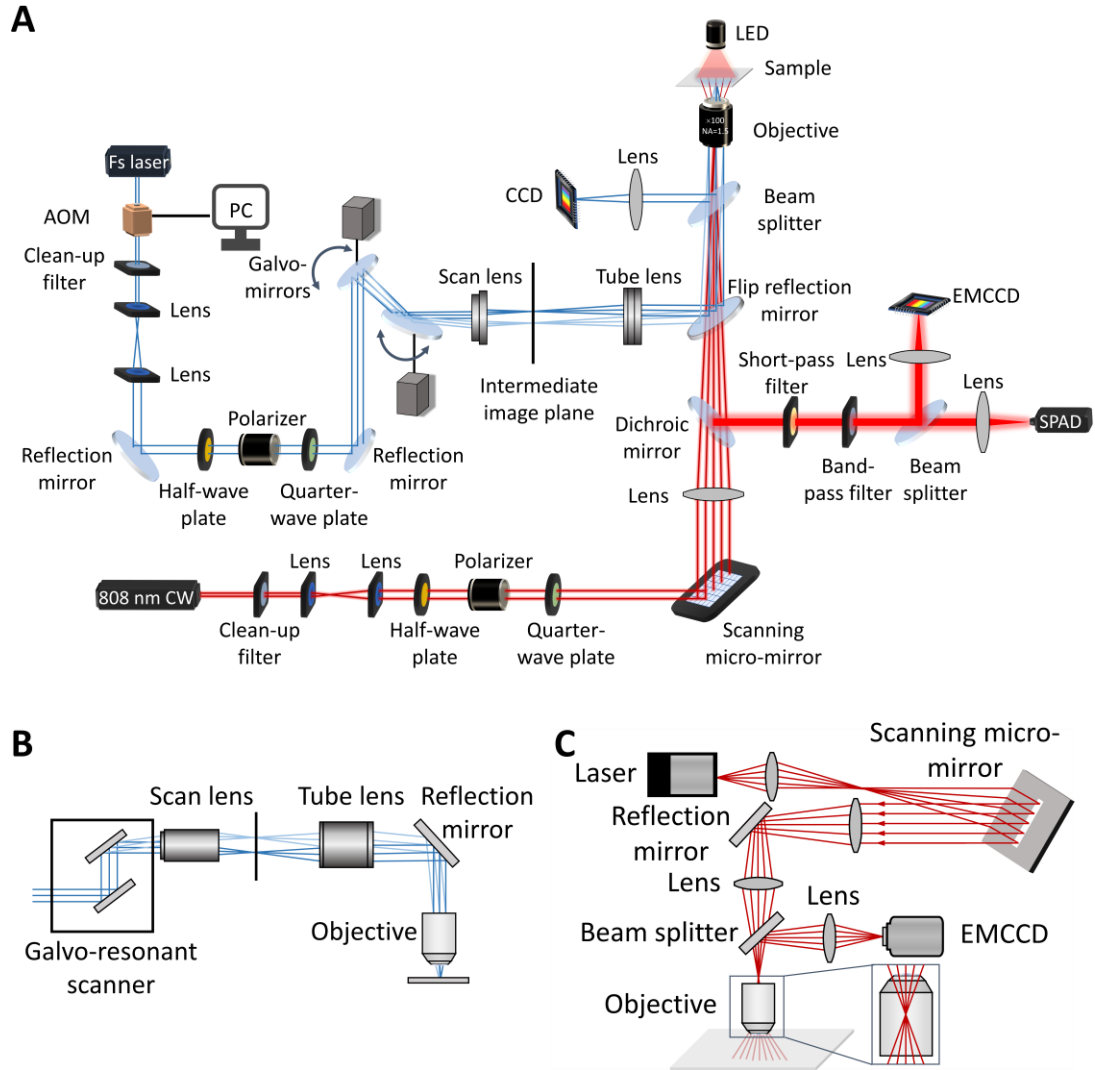
repeated read/write cycles. These strategies outline a pathway toward scalable, high-density 3D ODS using polymer-based volumetric media (**Table S4**).

Supplementary Figures

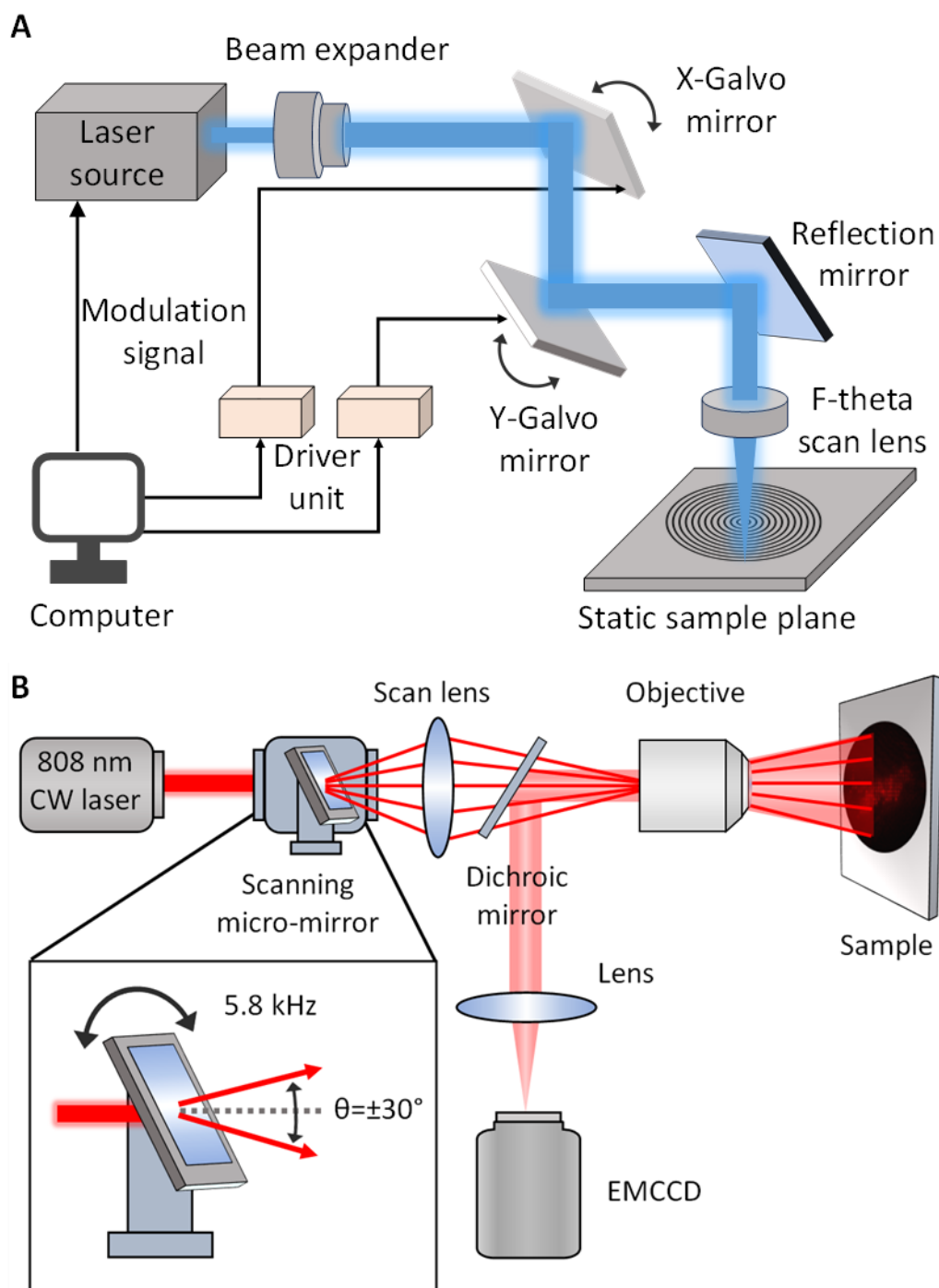
I. Optical Systems and Experimental Methodologies



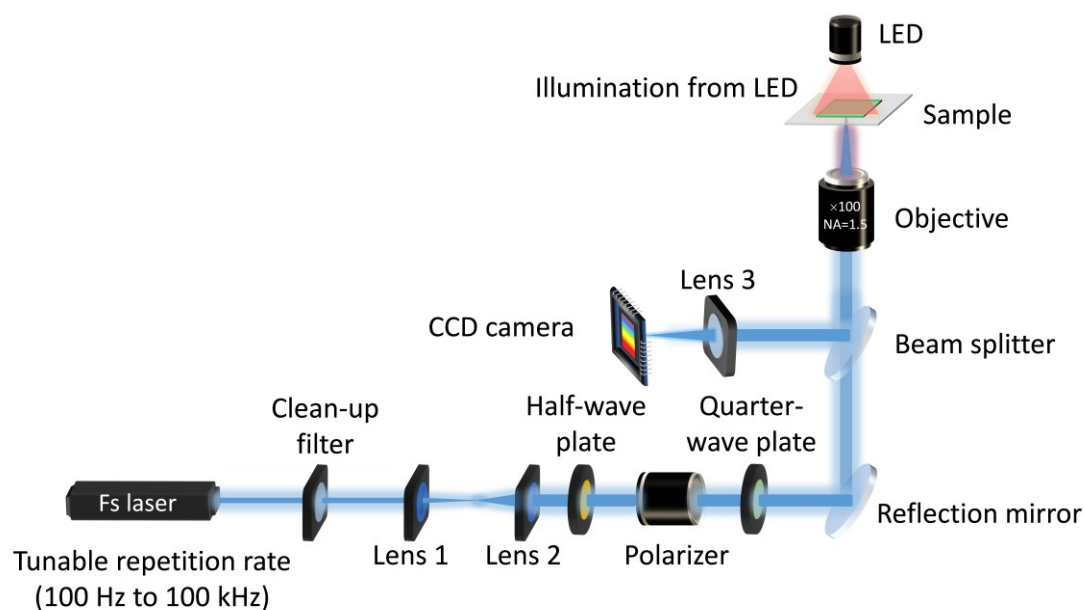
Supplementary fig 1. Confocal *in situ* writing–readout system. Schematic of the confocal microscopy platform used for fs laser writing and CW readout of UCPL signals. A high-NA objective focuses the excitation beam, while a dichroic mirror separates excitation and emission paths. UCPL signals are detected by a SPAD using notch and short-pass optical filters. LED: light-emitting diode; CCD: charge-coupled device; SPAD: single-photon avalanche diode.



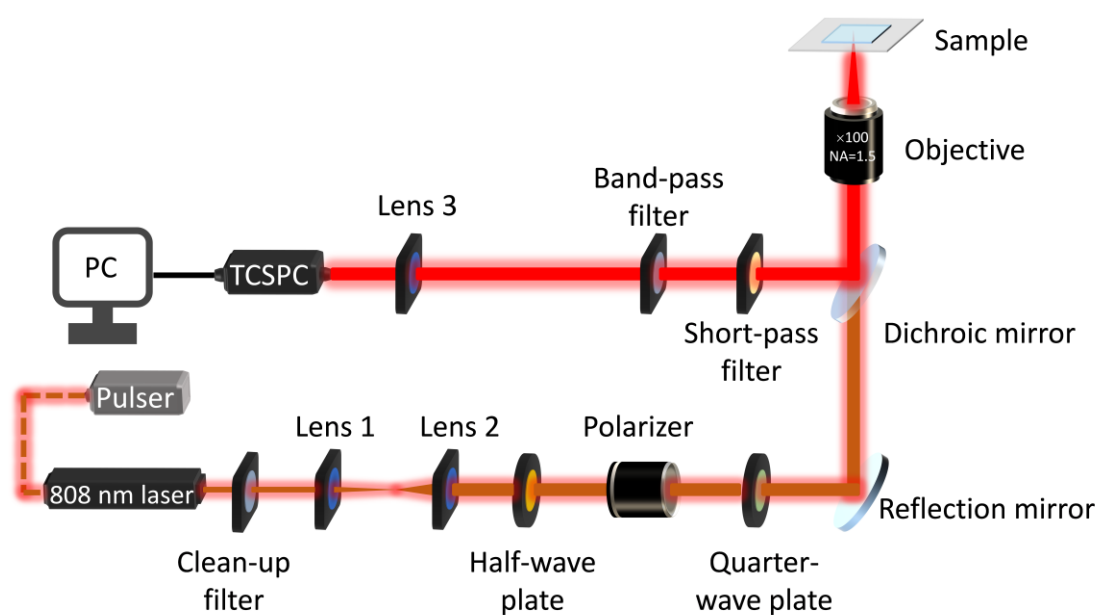
Supplementary fig 2. GS laser writing and wide-field readout system. (A) Schematic of the GS configuration used for large-area laser patterning and wide-field UCPL detection. (B) Detailed layout of the GS laser-writing module. (C) Configuration of the wide-field readout module. Emission signals are collected by an EMCCD through dichroic mirrors and optical filters. AOM: acousto-optic modulator; EMCCD: electron-multiplying charge-coupled device.



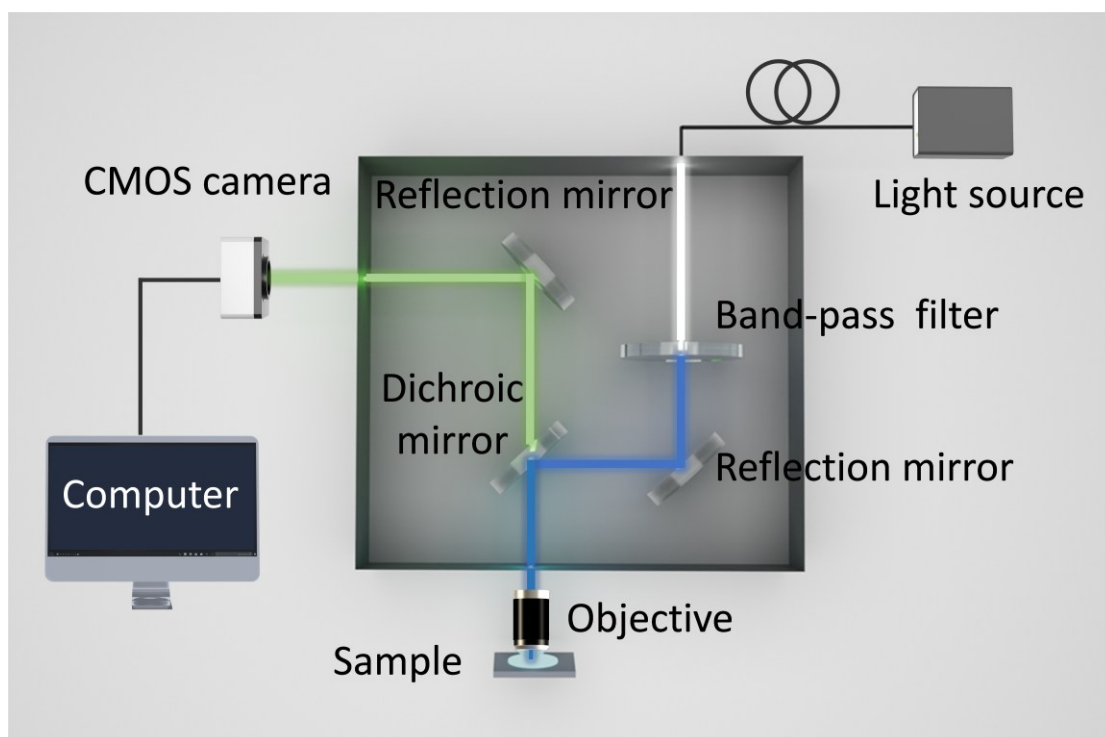
Supplementary fig 3. Dynamic laser writing and readout configuration. (A) Configuration incorporating X–Y galvo mirrors and an F-theta scan lens for rapid beam steering and precise spatial control during fs-laser patterning. (B) Wide-field readout configuration using an 808 nm CW excitation laser and EMCCD detection. The inset shows the galvo mirror scanning mechanism with an angular range of $\pm 30^\circ$ and a maximum scanning frequency of 5.8 kHz.



Supplementary fig 4. Writing time-response characterization. Schematic of the fs-laser writing kinetics measurement setup incorporating an optical shutter and a piezoelectric positioning stage. The formation dynamics of u-CPDs generated during fs-laser irradiation in the PEGDA-based photo-polymer matrix is investigated by adjusting the laser repetition frequency to control the number of pulses delivered to the sample.

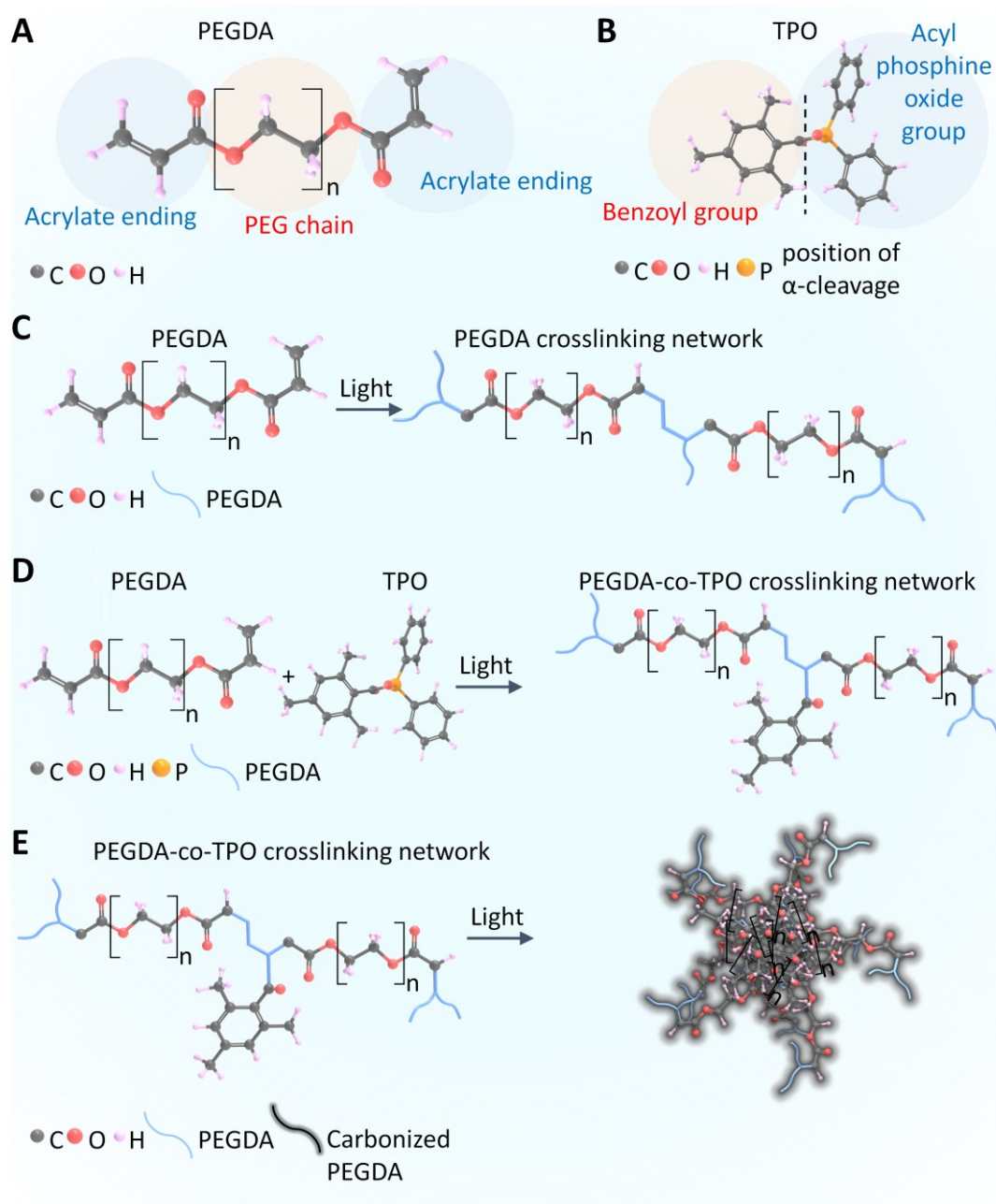


Supplementary fig 5. Readout time-response characterization. Schematic diagram of the UCPL lifetime measurement setup based on an 808 nm pulsed excitation source and time-resolved detection. This configuration enables measurement of UCPL decay kinetics during optical readout, allowing precise characterization of the lifetime dynamics of laser-written upconversion structures.

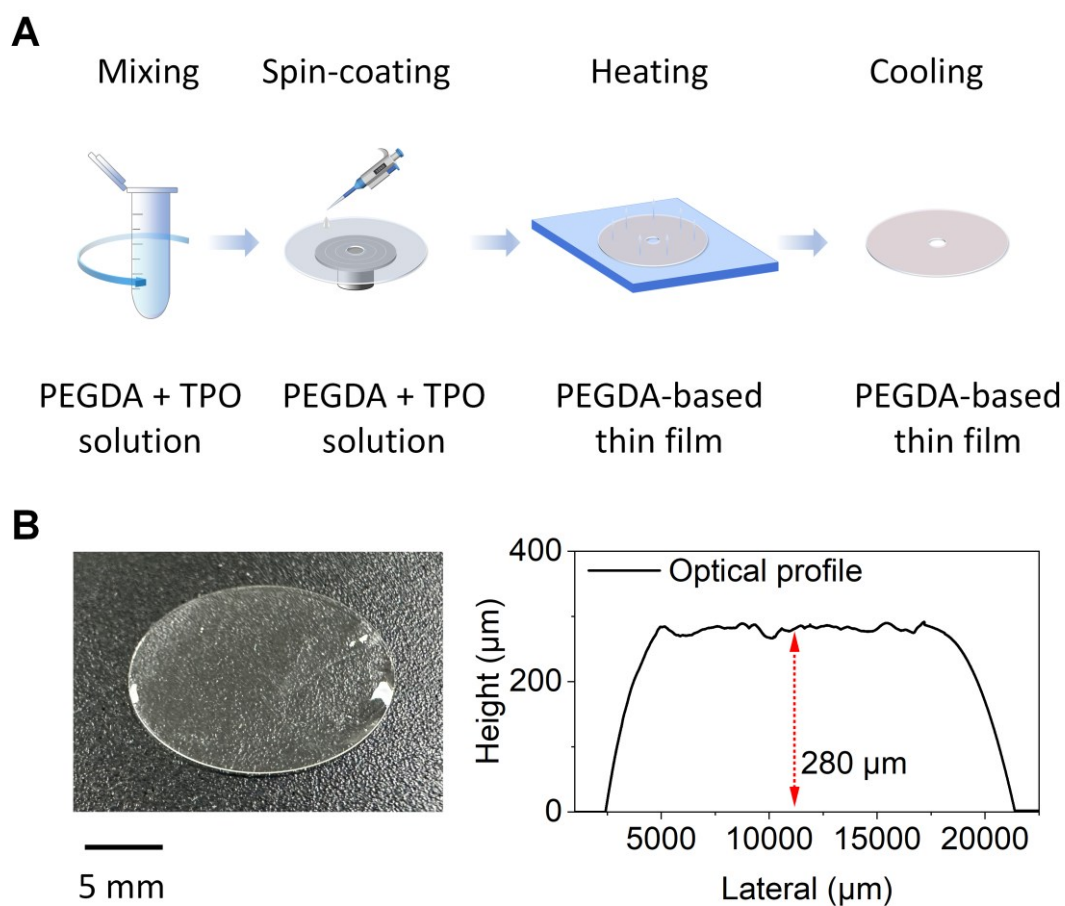


Supplementary fig 6. Wide-field DCF imaging system. Schematic illustration of the wide-field fluorescence imaging system used for DCF detection. Fluorescence emission is excited using an LED light source and recorded by an sCMOS camera. Optical filters suppress excitation leakage and improve the signal-to-noise ratio.

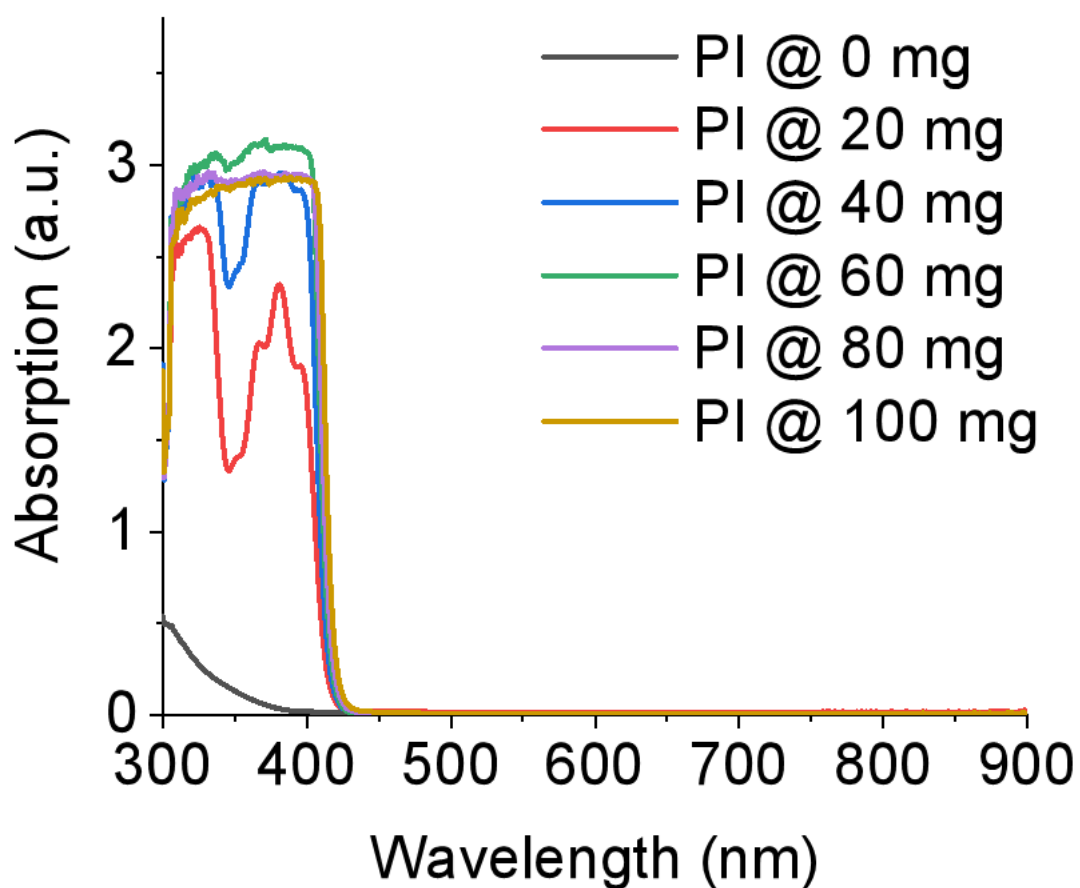
II. Materials Chemistry and Thin-Film Fabrication



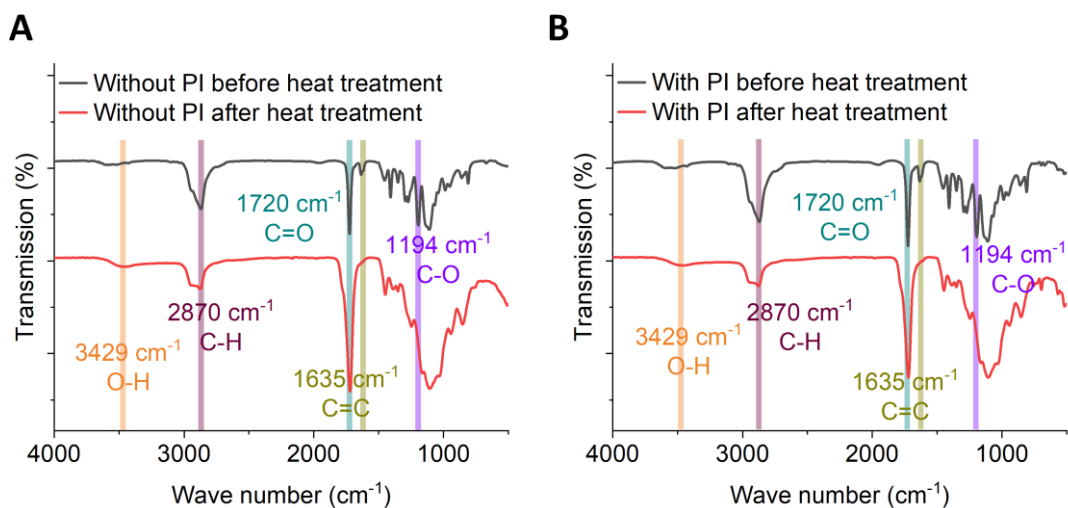
Supplementary fig 7. PEGDA photo-polymer photochemistry. (A) Molecular structure of PEGDA as a photo-monomer. (B) Molecular structure of TPO as a PI. (C) Cross-linking reaction of PEGDA to form a PEGDA cross-linking network under light exposure. (D) Cross-linking reaction of PEGDA and TPO to form a PEGDA-co-TPO cross-linking network under light exposure. (E) Carbonization reactions of a PEGDA-co-TPO cross-linking network under light exposure.



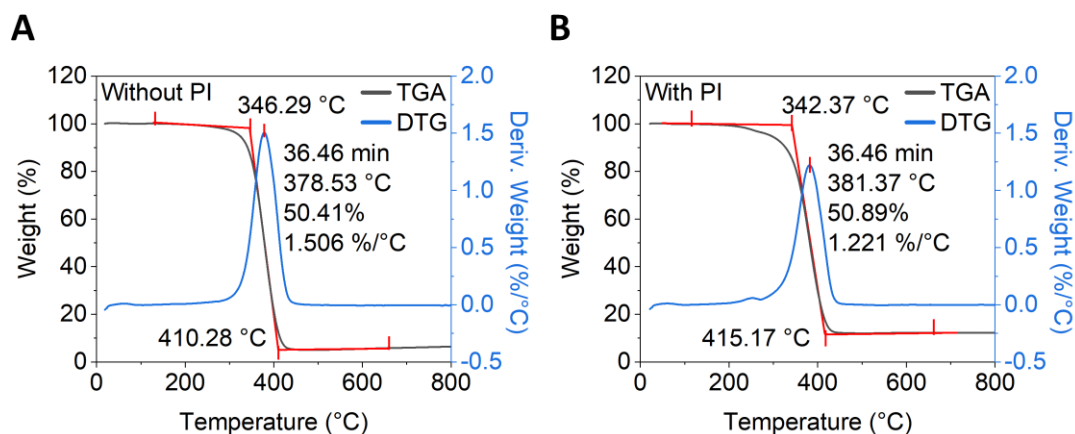
Supplementary fig 8. Fabrication of PEGDA thin films. (A) Synthesis and fabrication of the PEGDA-based photo-polymer thin film. A solution of PEGDA and TPO is dispensed onto a glass coverslip using a micro-pipette and spin-coated. After coating, the sample is heated on a hot plate and then left to cool naturally to room temperature. (B) Photograph (left) and step-height measurement (right) of the PEGDA-based photo-polymer thin film on a coverslip.



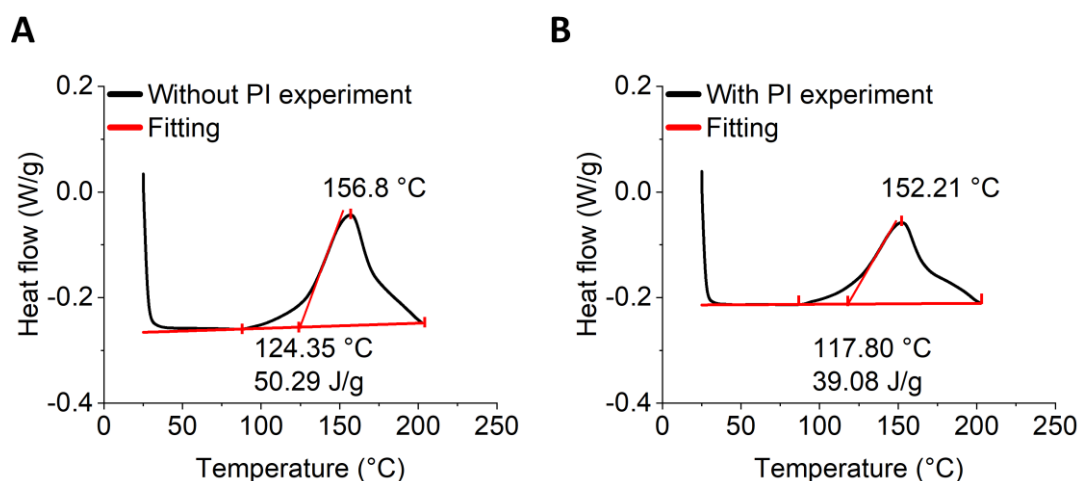
Supplementary fig 9. UV-vis absorption spectra. UV-vis absorption spectra of the PEGDA-based photo-polymer thin film before and after incorporating different amounts of TPO as a PI, illustrating the changes in optical absorption introduced by the initiator molecules.



Supplementary fig 10. FTIR spectra of PEGDA films. (A) FTIR spectra of the PEGDA-based photo-polymer thin films without PI before and after heat treatment. (B) FTIR spectra of the PEGDA-based photo-polymer thin film with PI before and after heat treatment, showing chemical bonding changes associated with polymer cross-linking.

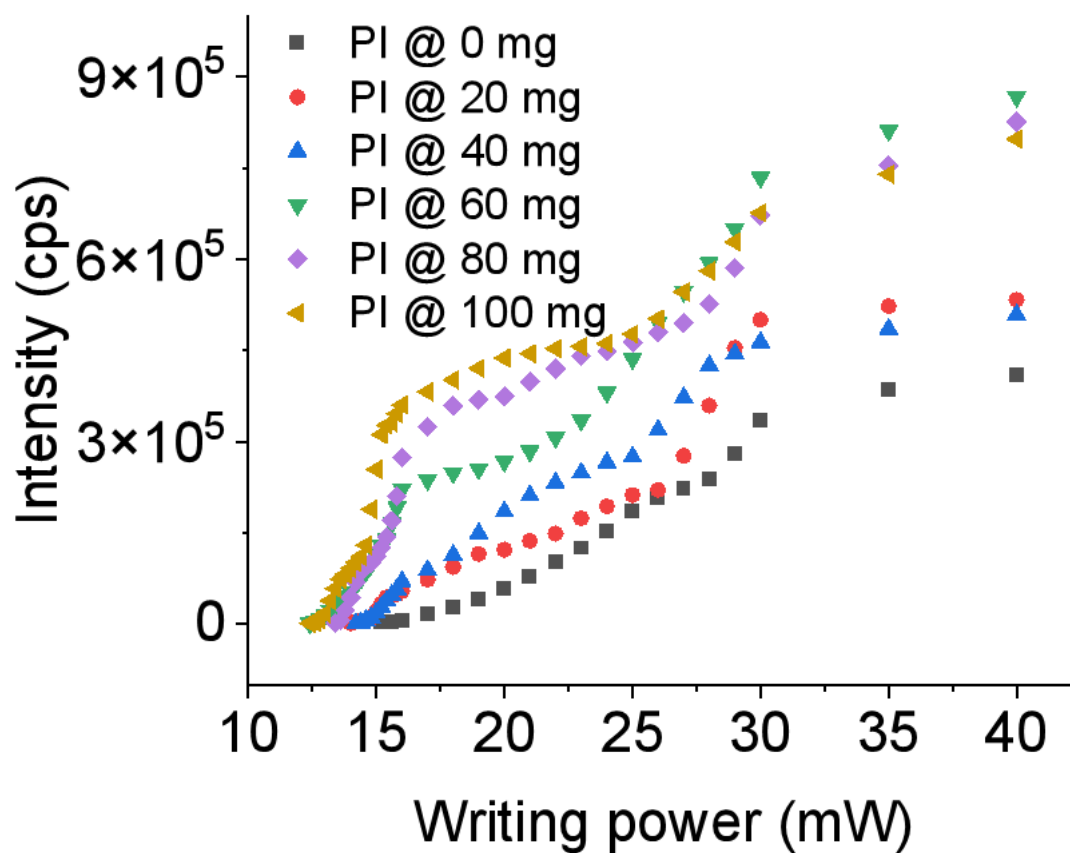


Supplementary fig 11. Thermal stability of PEGDA films. TGA curves of PEGDA-based photo-polymer thin films obtained (A) without PI and (B) with PI. The measurements reveal the thermal decomposition behavior and stability of the polymer films under elevated temperature conditions.

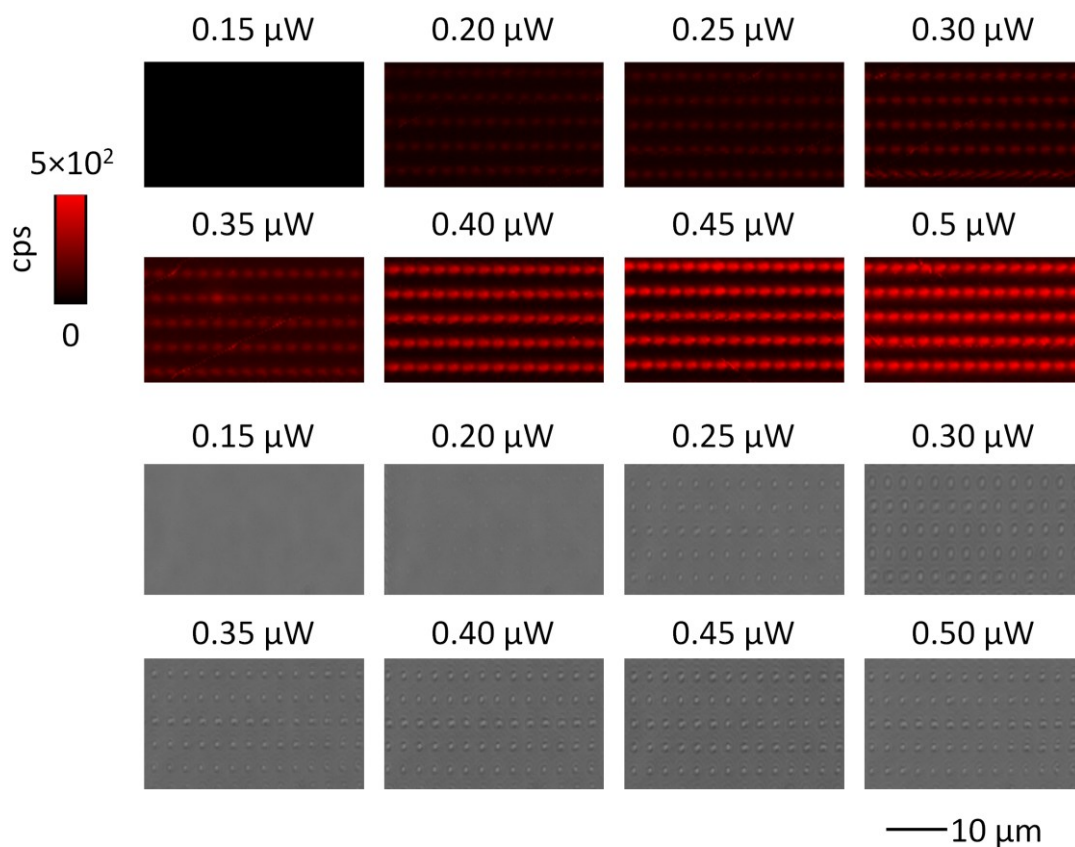


Supplementary fig 12. DSC analysis. DSC curves of PEGDA photo-polymer films recorded (A) without PI and (B) with PI. The data provide information on thermal transitions and polymer network formation within the PEGDA-based photo-polymer system.

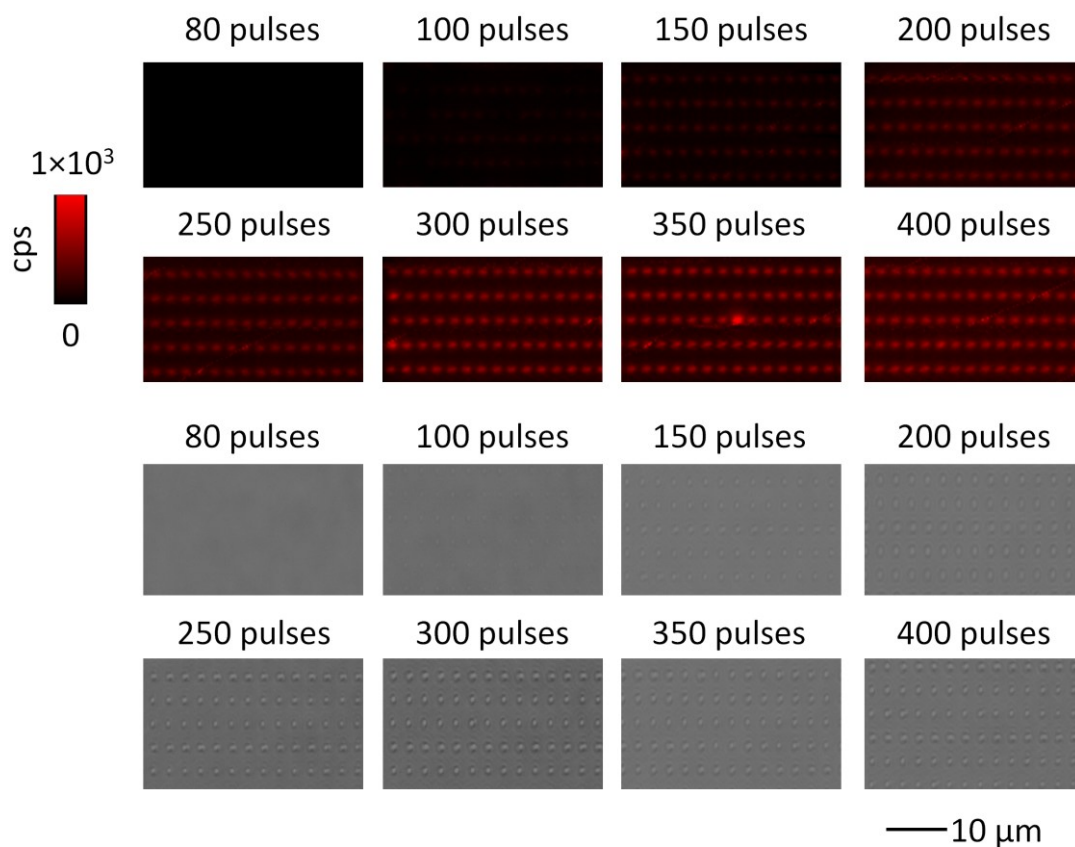
III. Fs-Laser Writing Thresholds and Carbonization Kinetics



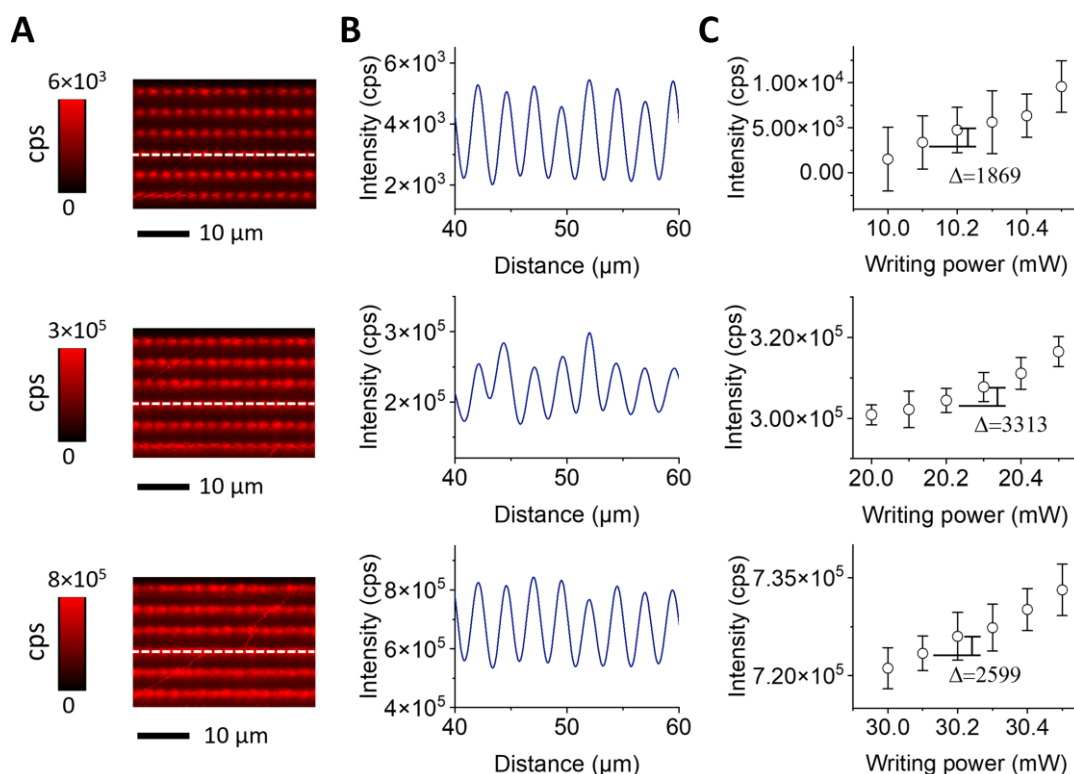
Supplementary fig 13. UCPL response of PEGDA films. UCPL intensity of PEGDA-based photo-polymer thin films without and with the PI at various concentrations under irradiation with an 808 nm CW laser, following irradiation to a 460 nm fs laser at varying power levels.



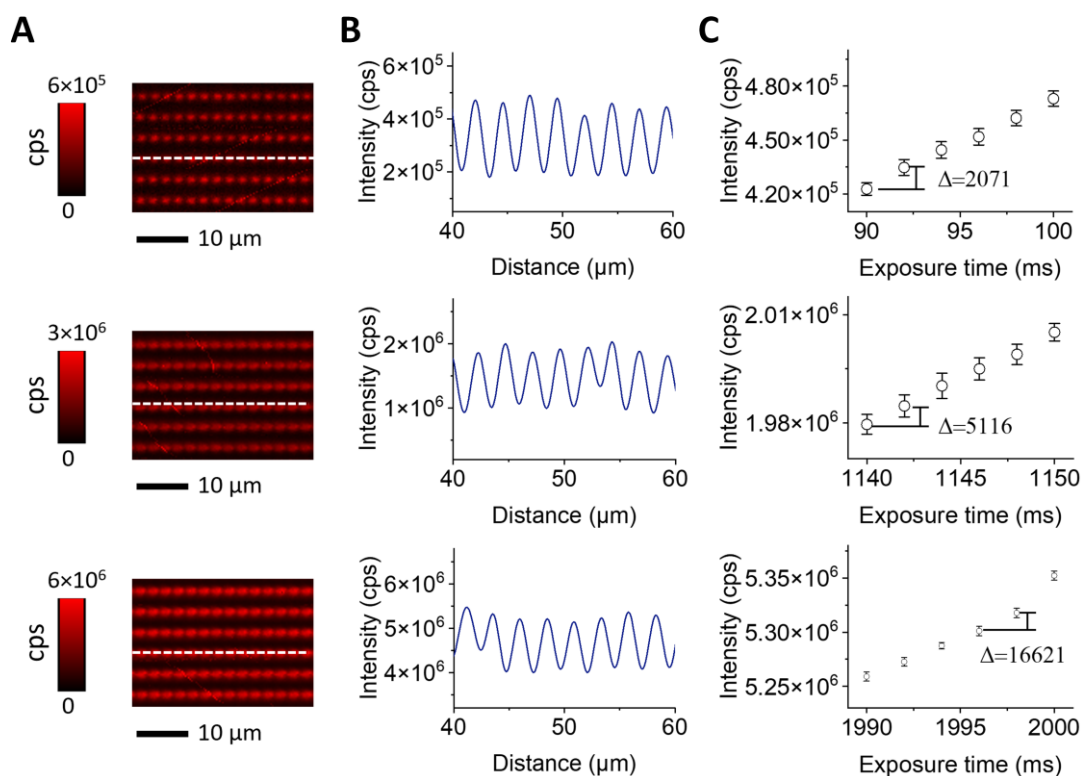
Supplementary fig 14. Laser-power-dependent u-CPDs formation. Confocal UCPL images (top) and bright-field optical images (bottom) of u-CPDs written with a single pulse at different fs-laser power levels. The images reveal threshold behavior and morphological changes associated with increasing irradiation energy.



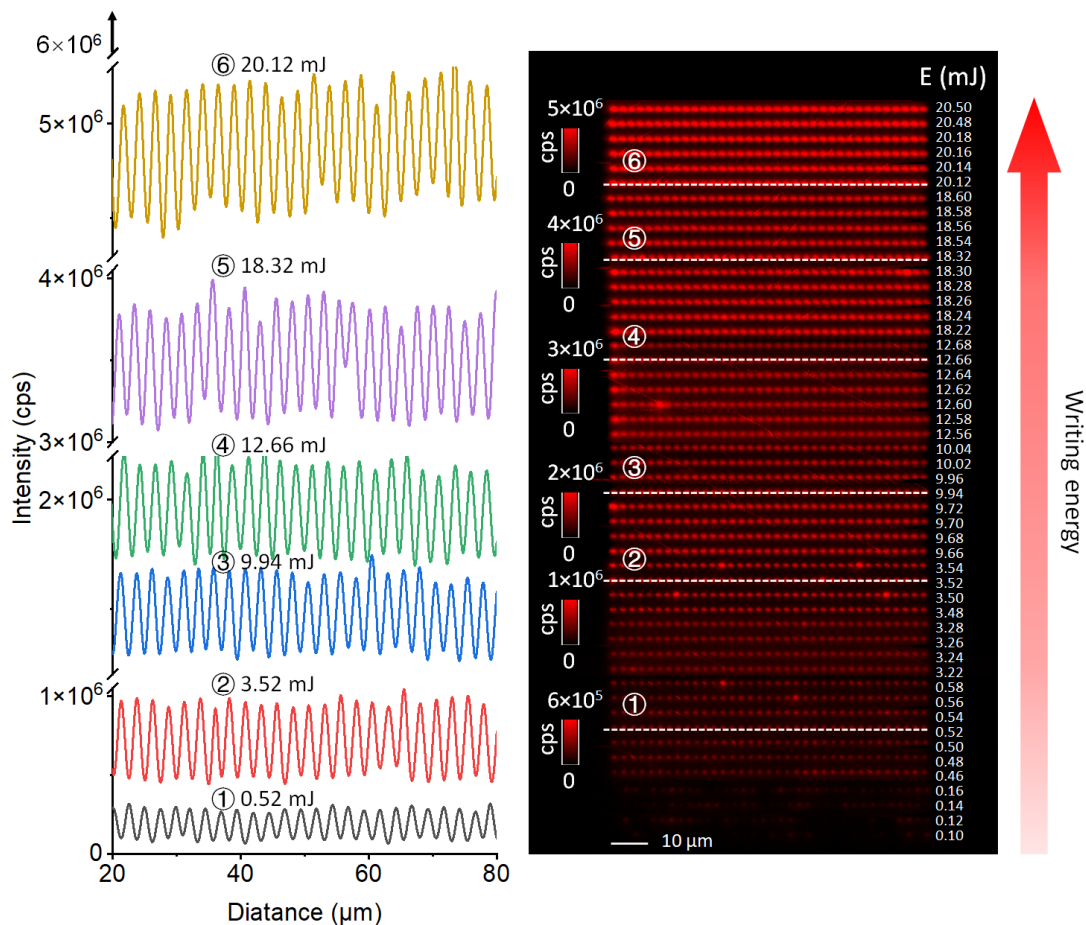
Supplementary fig 15. Pulse-number-dependent u-CPDs formation. Confocal UCPL images (top) and corresponding bright-field optical images (bottom) of u-CPDs generated with different pulse numbers while maintaining a constant laser power of 0.15 μW . These results demonstrate the influence of pulse accumulation on nanoscale carbonization.



Supplementary fig 16. Power-dependent UCPL imaging. (A) Confocal optical microscopy imaging of optical data bit patterns in the PEGDA-based photo-polymer with PI by detecting UCPL under irradiation with an 808 nm CW laser at a power of 1 mW and pixel dwell time of 5 ms following irradiation to a 460 nm fs laser at varying power levels of 10-10.5 mW (top), 20-20.5 mW (middle), and 30-30.5 mW (bottom) and fixed exposure time of 10 ms. (B) UCPL intensity profiles of the optical data bit patterns corresponding to the white dashed lines in (A). (C) UCPL intensity of optical data bit patterns in (A) under 808 nm CW laser at a power of 1 mW and a 460 nm fs laser at varying power levels of 10-10.5 mW (top), 20-20.5 mW (middle), and 30-30.5 mW (bottom) and fixed exposure time of 10 ms.

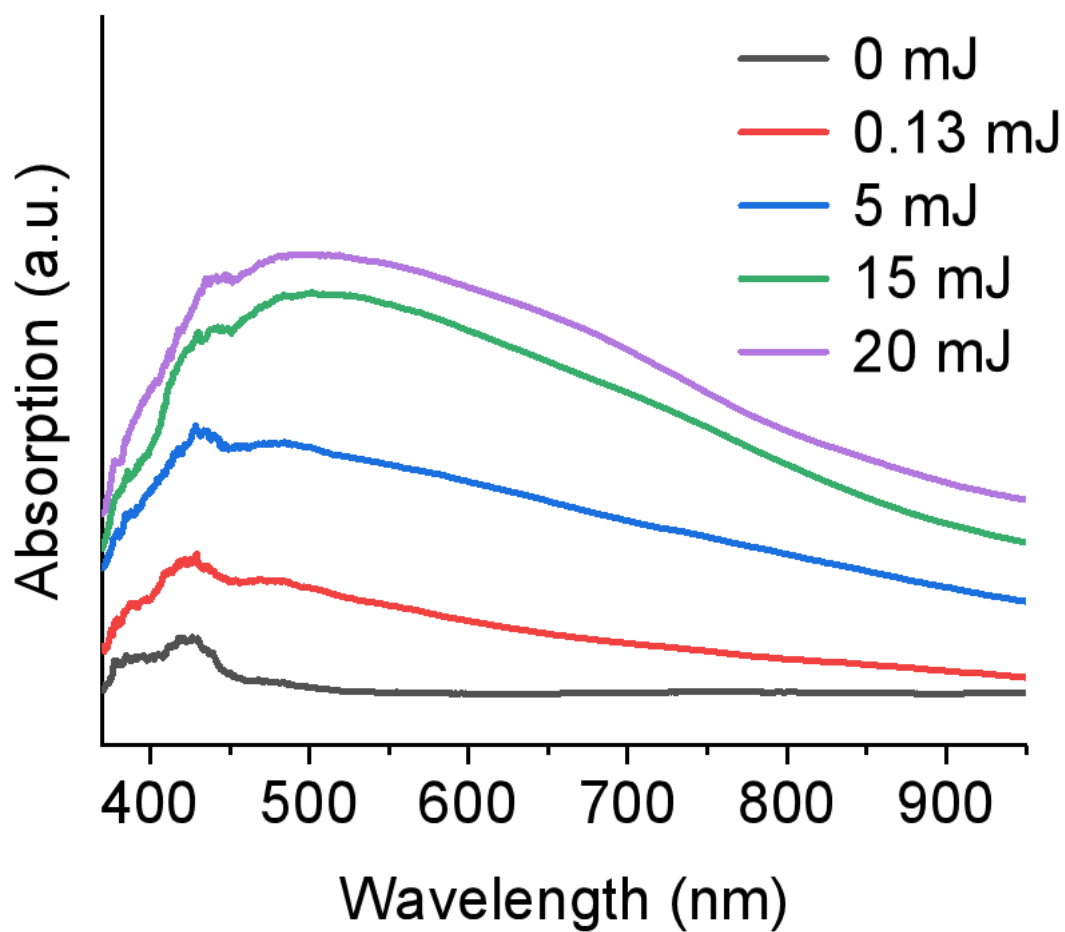


Supplementary fig 17. Exposure-time-dependent UCPL imaging. (A) Confocal optical microscopy imaging of optical data bit patterns in the PEGDA-based photopolymer with PI by detecting UCPL under irradiation with an 808 nm CW laser at a power of 1 mW and pixel dwell time of 5 ms following irradiation to a 460 nm fs laser at varying exposure times of 90-100 ms (top), 1,140-1,150 ms (middle), and 1,990-2,000 ms (bottom) and fixed power of 10 mW. (B) UCPL intensity profiles of the optical data bit patterns corresponding to the white dashed lines in (A). (C) UCPL intensity of optical data bit patterns in (A) under 808 nm CW laser at a power of 1 mW and a 460 nm fs laser at varying exposure times of 90-100 ms (top), 1,140-1,150 ms (middle), and 1,990-2,000 ms (bottom) and fixed power of 10 mW.

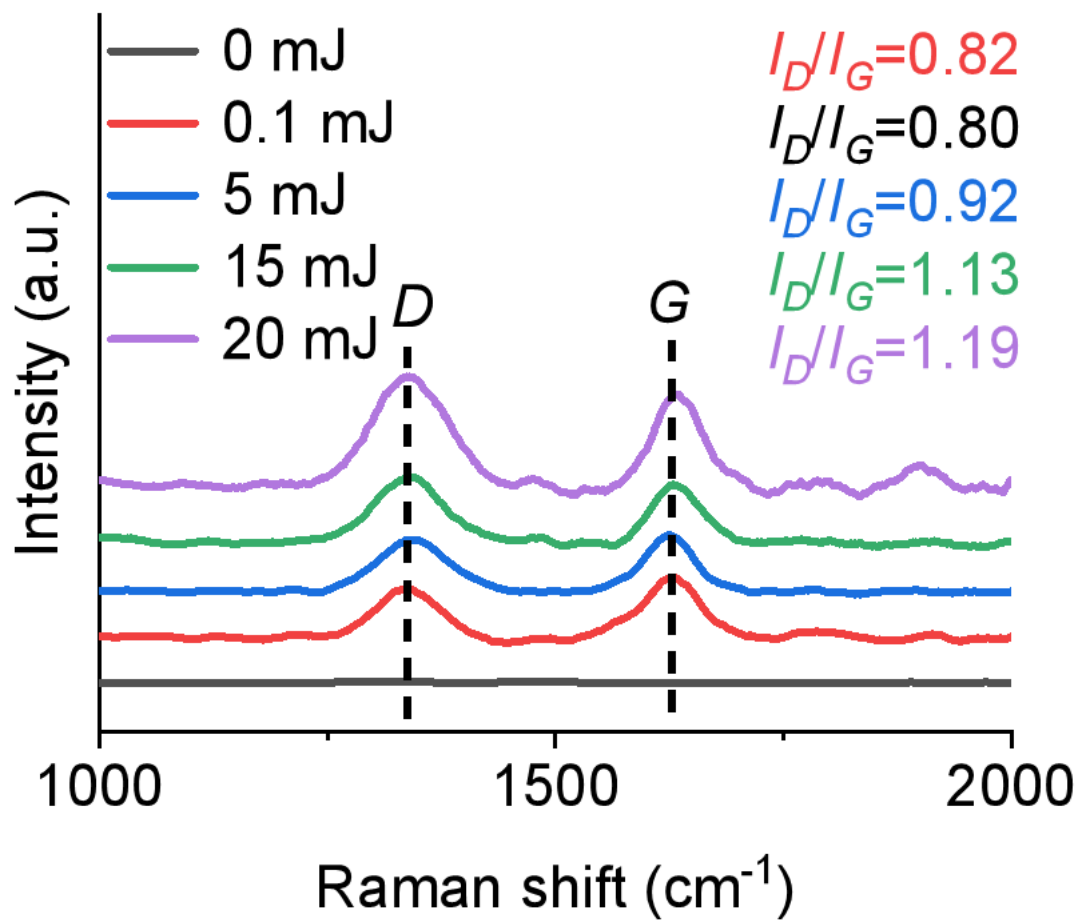


Supplementary fig 18. Energy-dose-dependent UCPL signals. Confocal optical microscopy imaging and corresponding intensity profiles of optical data bit patterns in the PEGDA-based photo-polymer with PI by detecting UCPL under irradiation with an 808 nm CW laser at a power of 1 mW and pixel dwell time of 5 ms following irradiation to a 460 nm fs laser at varying energy doses of 0.1 mJ to 20.5 mJ (from top to bottom).

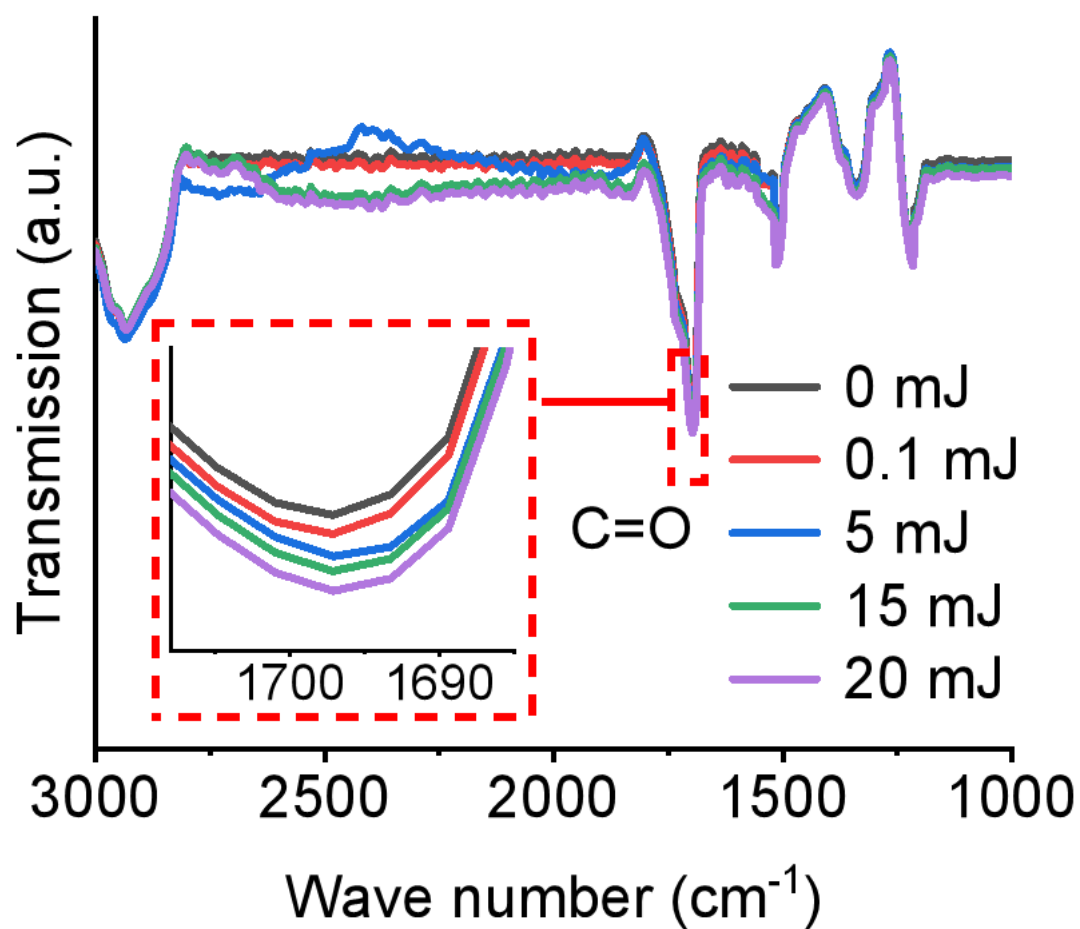
IV. Spectroscopic Evidence of Photo-Carbonization



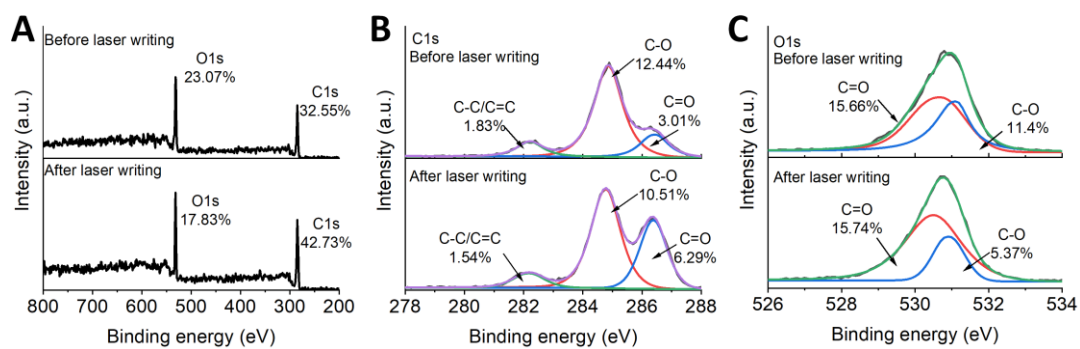
Supplementary fig 19. Micro-absorption spectra. Micro-absorption spectroscopy of the PEGDA-based photo-polymer without PI before and after irradiation with a 460 nm fs laser at various energy doses.



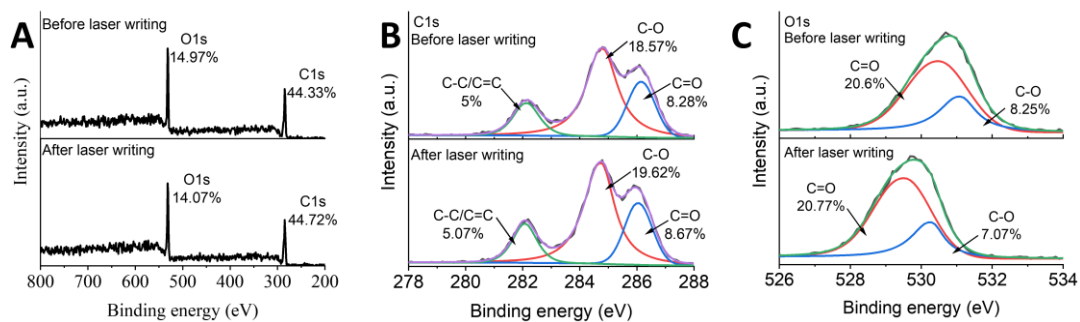
Supplementary fig 20. Micro-Raman spectra. Micro-Raman spectroscopy of the PEGDA-based photo-polymer without PI before and after irradiation with a 460 nm fs laser at various energy doses.



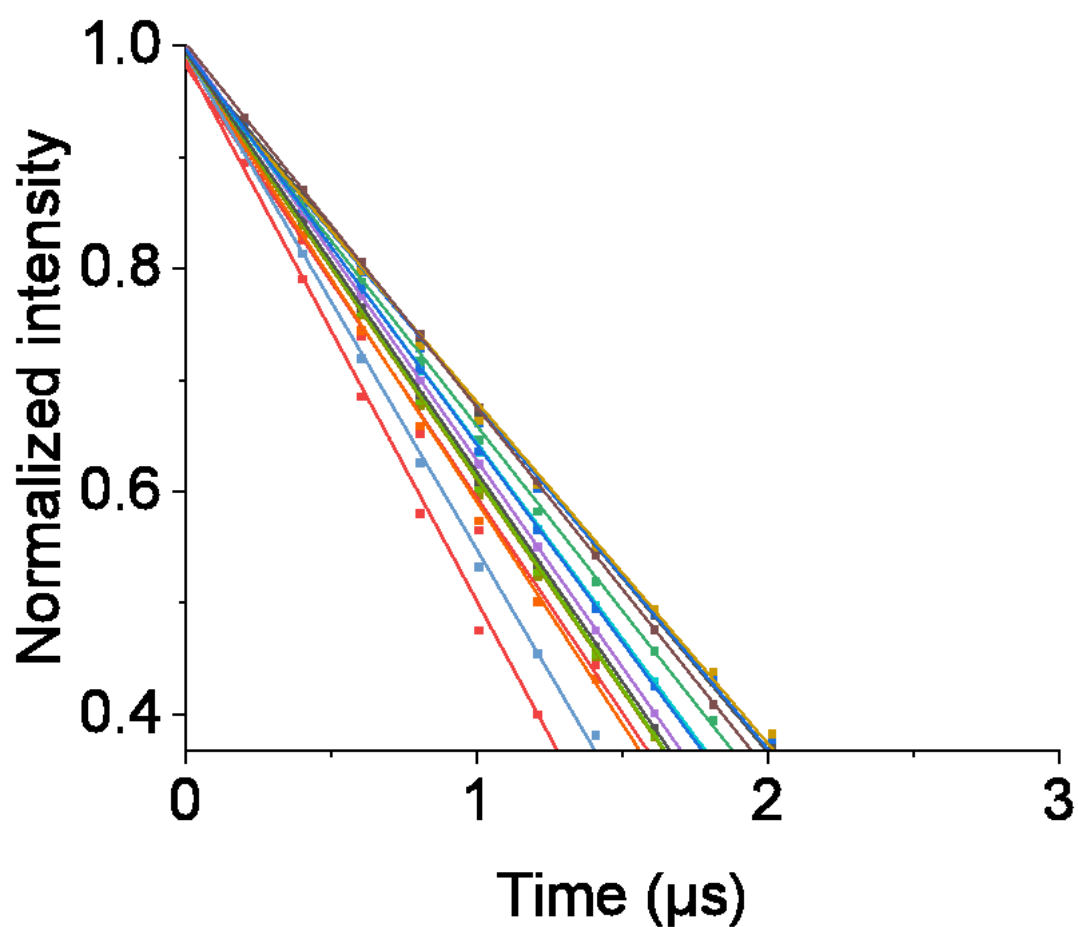
Supplementary fig 21. Micro-FTIR spectra. Micro-FTIR spectroscopy of the PEGDA-based photo-polymer without PI before and after irradiation with a 460 nm fs laser at various energy doses.



Supplementary fig 22. XPS characterization. (A) High-resolution wide-scan, (B) C1s, and (C) O1s XPS spectra of the PEGDA-based photo-polymer without PI before and after irradiation with a 460 nm fs laser.

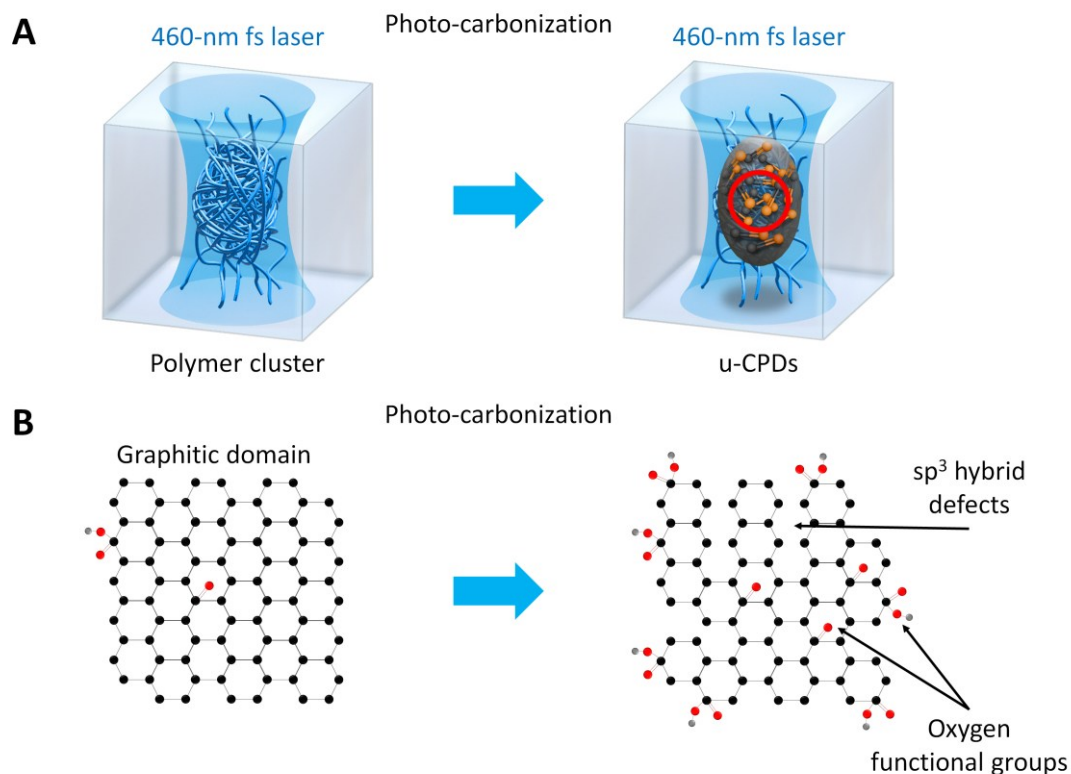


Supplementary fig 23. XPS characterization. (A) High-resolution wide-scan, (B) C1s, and (C) O1s XPS spectra of the PEGDA-based photo-polymer with PI before and after irradiation with a 460 nm fs laser.

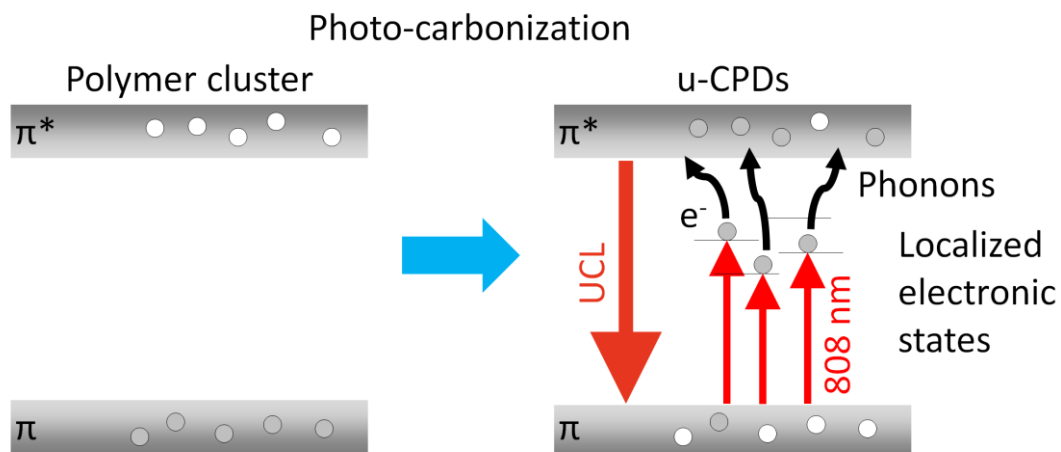


Supplementary fig 24. UCPL lifetimes of u-CPDs measured under pulsed 808 nm excitation. Measurements were obtained from different spatial locations within regions written by the 460 nm fs laser, demonstrating the spatial uniformity and reproducibility of UCPL emission across the patterned structures.

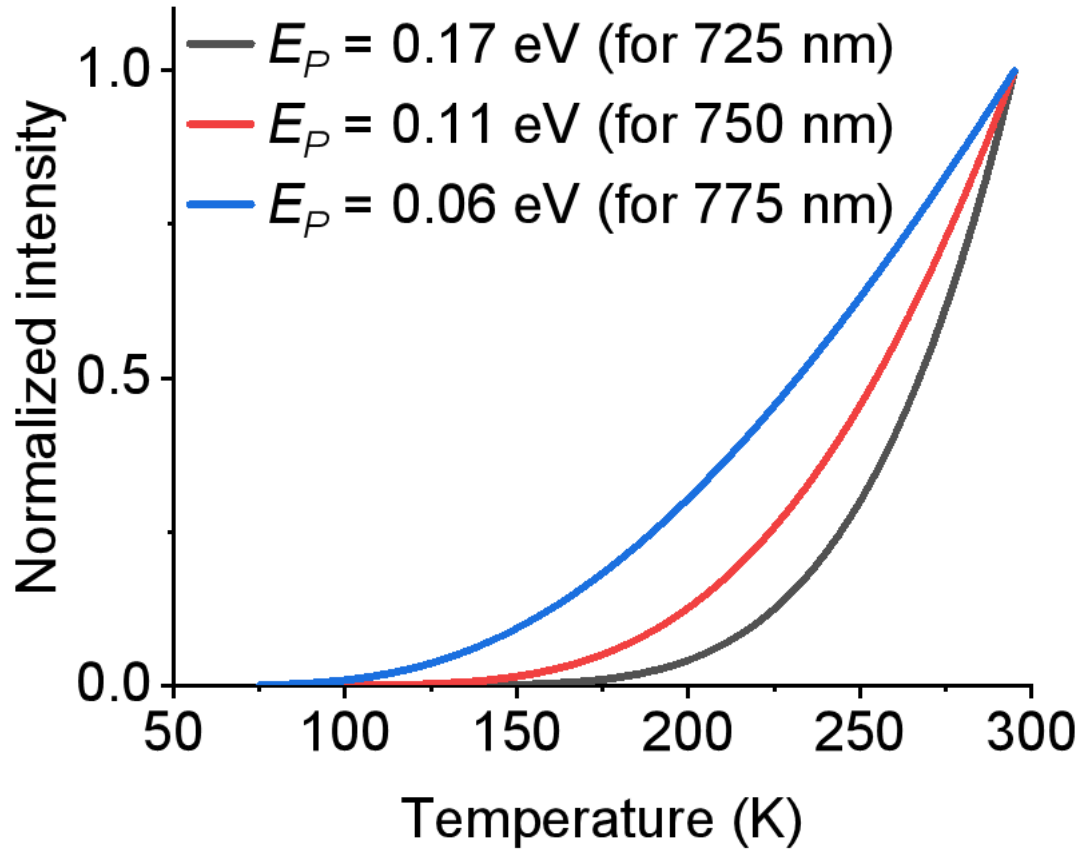
V. UCPL Mechanism and Photophysics



Supplementary fig 25. Photo-carbonization mechanism. (A) Schematic of the proposed mechanism of photo-carbonization in a PEGDA-based photo-polymer under irradiation with a 460 nm fs laser, resulting in the formation of u-CPDs from polymer clusters. (B) Schematic of the proposed mechanism for the formation of graphitic domains with sp^3 hybrid defects and oxygen functional groups in u-CPDs during photo-carbonization of a PEGDA-based photo-polymer under irradiation with a 460 nm fs laser (shown as the inset of the red-circled area in (A)).

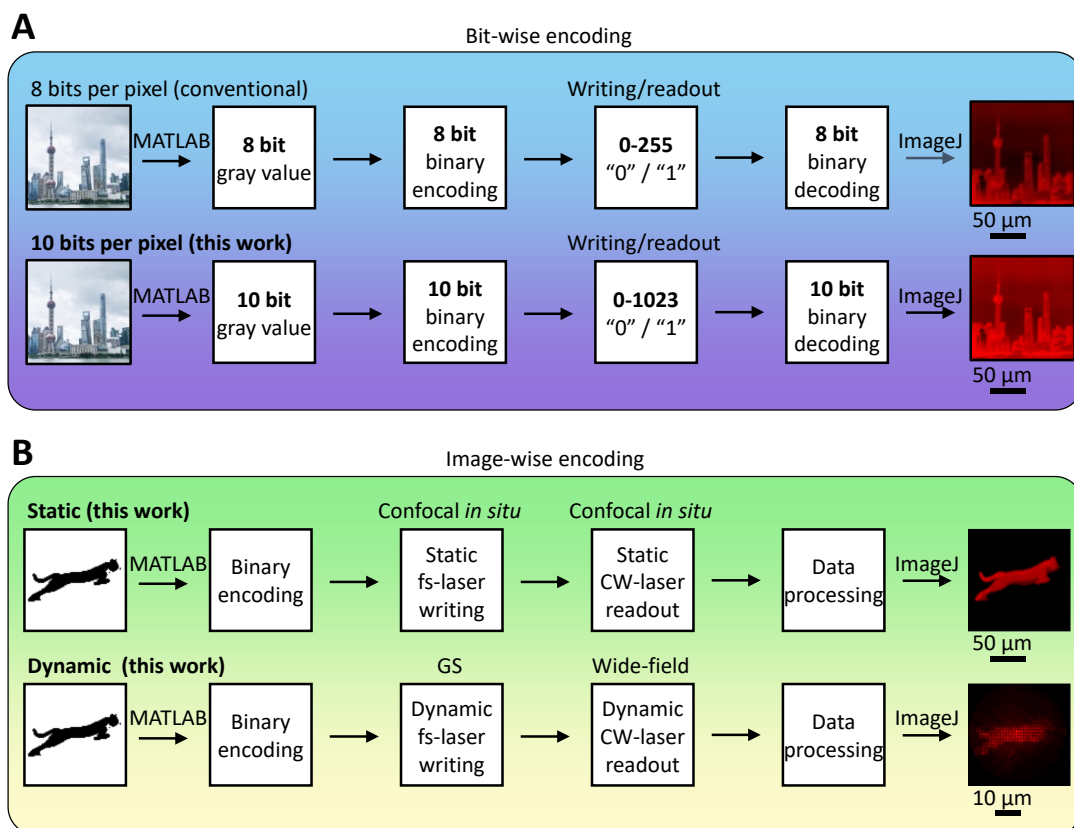


Supplementary fig 26. Phonon-assisted UCPL mechanism. Schematic of the proposed mechanism for the formation of phonon-assisted UCPL under excitation with an 808 nm CW laser, attributed to the formation of localized electronic states in graphitic domains with sp^3 hybrid defects and oxygen functional groups in u-CPDs during photo-carbonization of a PEGDA-based photo-polymer.

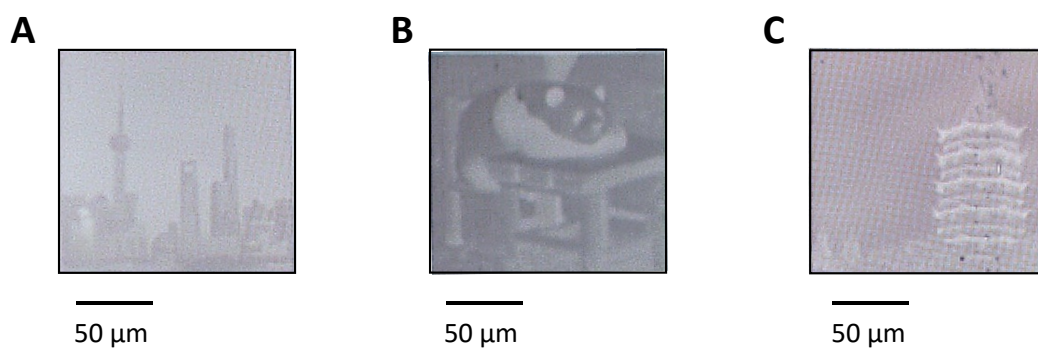


Supplementary fig 27. Simulated phonon-assisted UCPL intensity. Simulated normalized intensity of phonon-assisted UCPL influenced by the phonon population, which varies with temperature according to the Bose-Einstein distribution, for different phonon energies ($E_P = 0.17$ eV, 0.11 eV, 0.06 eV).

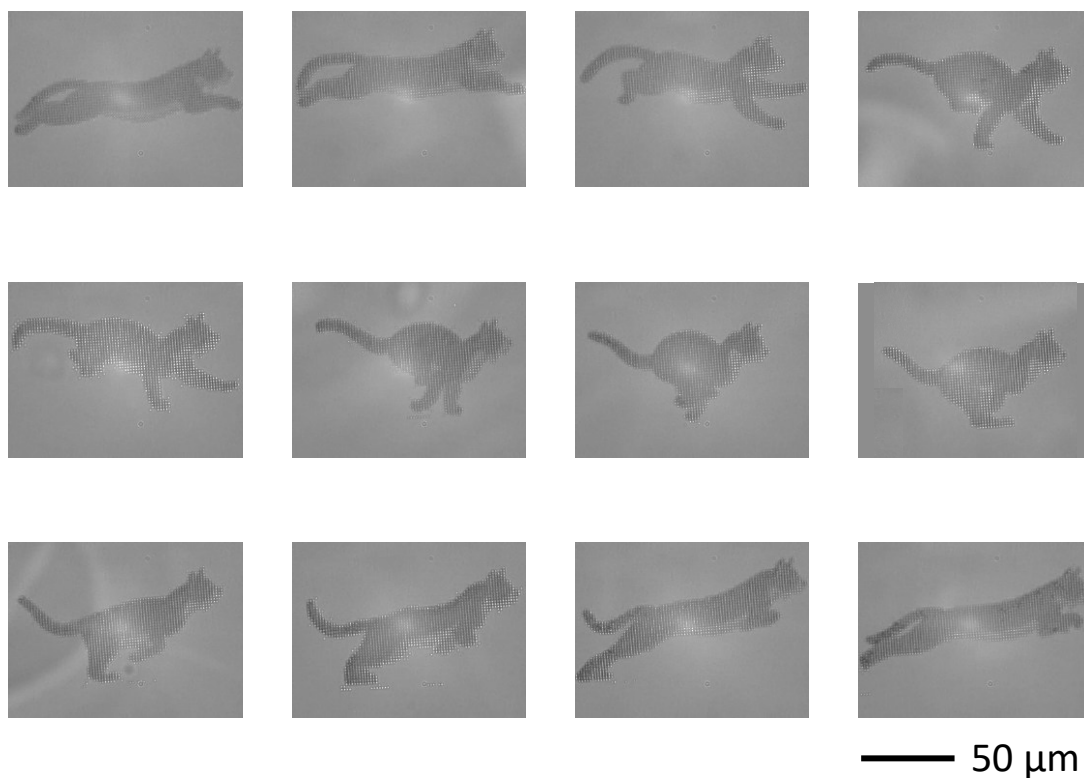
VI. Wide-Field Patterning and Parallel Readout



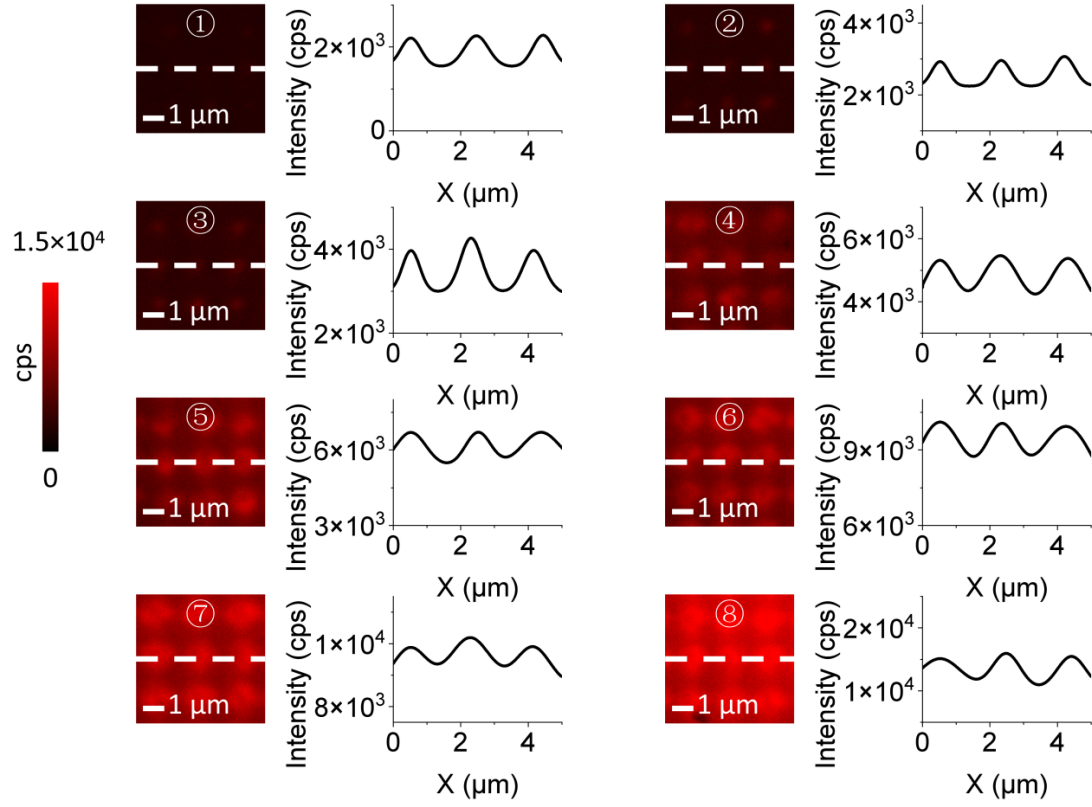
Supplementary fig 28. Optical data encoding workflow. (A) Comparison between conventional bitwise multilevel encoding (standard 8 bits per pixel) and the approach demonstrated in this work enabling up to 10 bits per pixel. (B) Illustration of the image-wise encoding strategies implemented in this study, including static confocal writing with confocal readout and dynamic GS-assisted writing combined with wide-field UCPL readout.



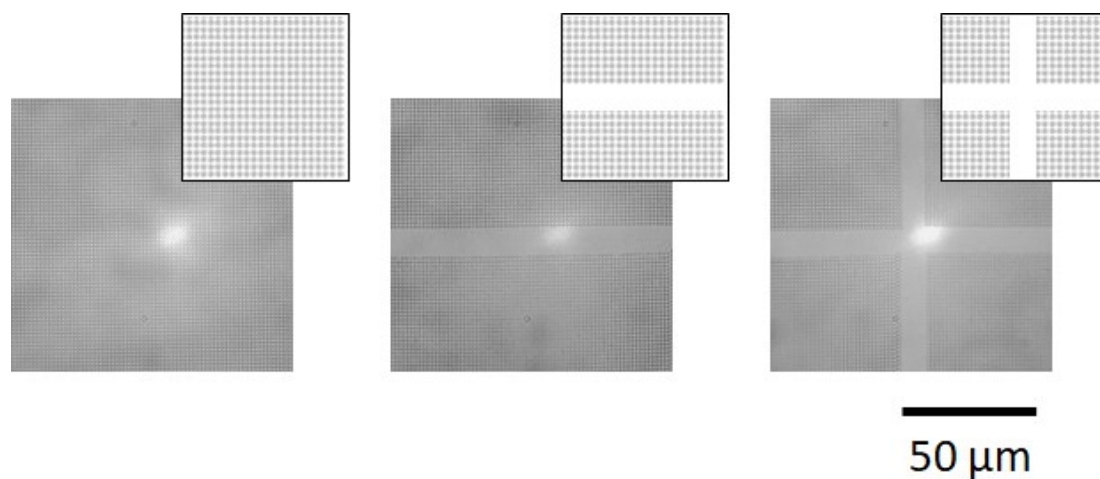
Supplementary fig 29. Bright-field optical microscopy images of microstructures patterned in PEGDA-based photo-polymer thin films. Optical patterns including (A) the Oriental Pearl Tower, (B) panda, and (C) the Suzhou Tower were fabricated using 460 nm fs-laser irradiation with exposure times ranging from 10 ms to 2200 ms at a fixed power of 10 mW.



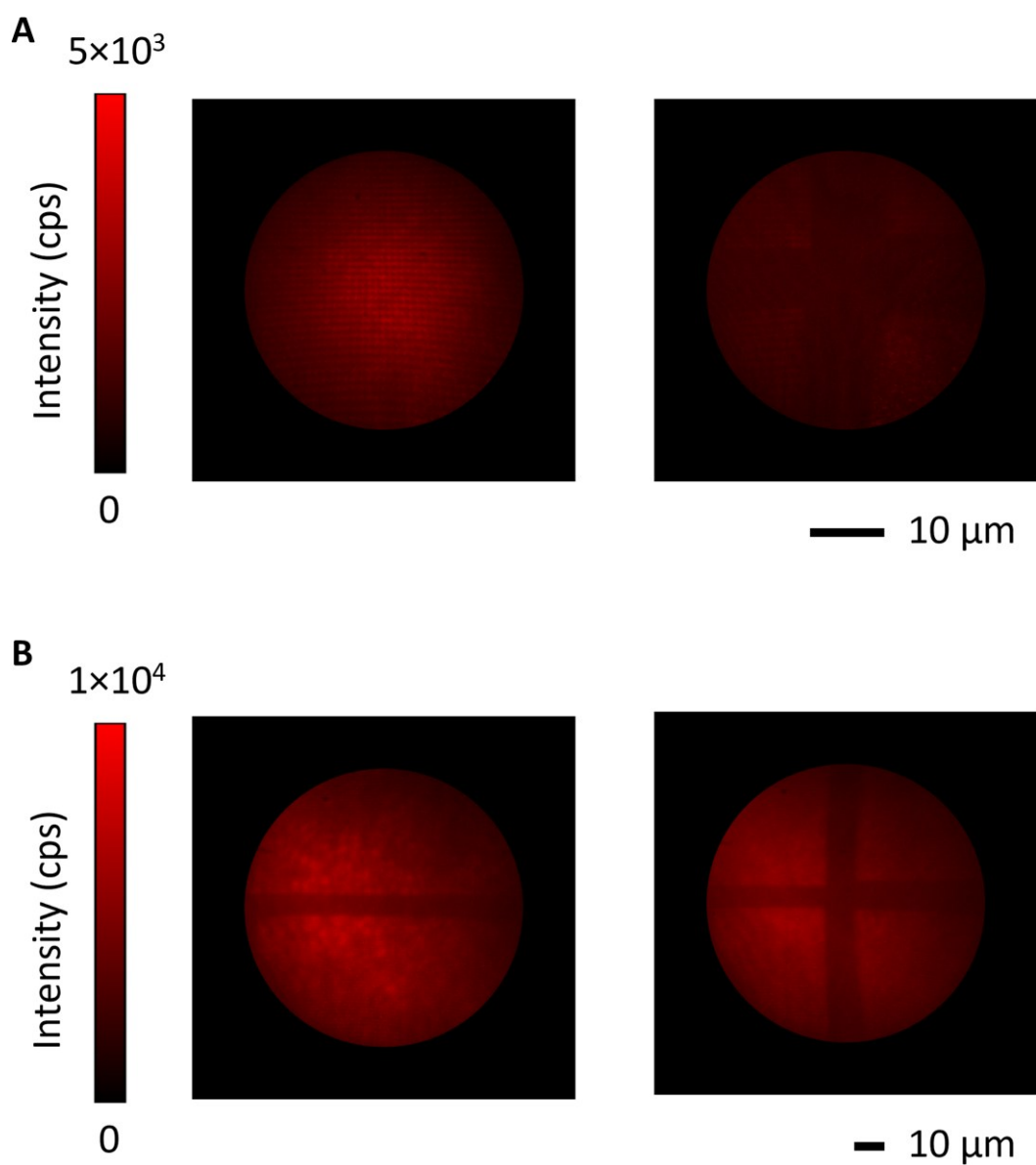
Supplementary fig 30. Running cat pattern written by confocal *in situ* laser writing. Bright-field optical microscopy images of a running cat pattern fabricated within PEGDA-based photo-polymer thin films using confocal *in situ* fs-laser writing. The images illustrate the spatial fidelity and resolution of laser-induced microstructures produced through localized photo-carbonization.



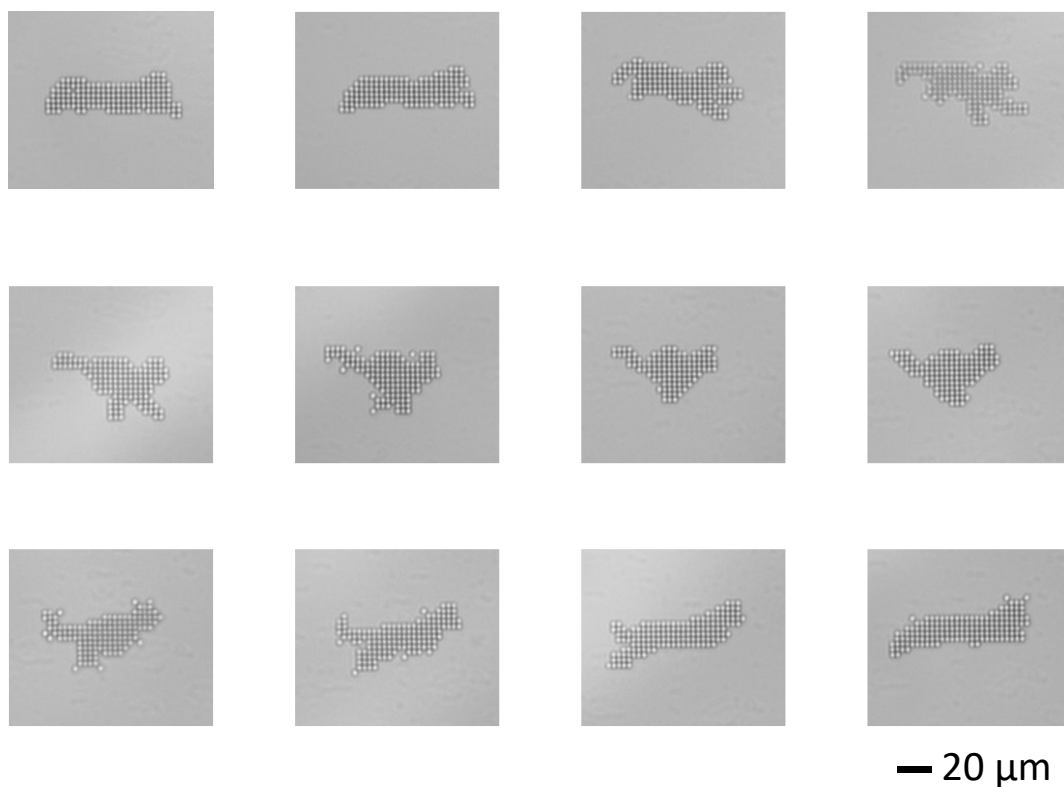
Supplementary fig 31. Wide-field UCPL emission images of optical data bits recorded at different laser exposure times in PEGDA-based photo-polymer thin films. Line intensity profiles extracted along the dashed line illustrate the modulation of UCPL intensity and confirm the spatial contrast of the recorded optical bits. Scale bar: $1\ \mu\text{m}$.



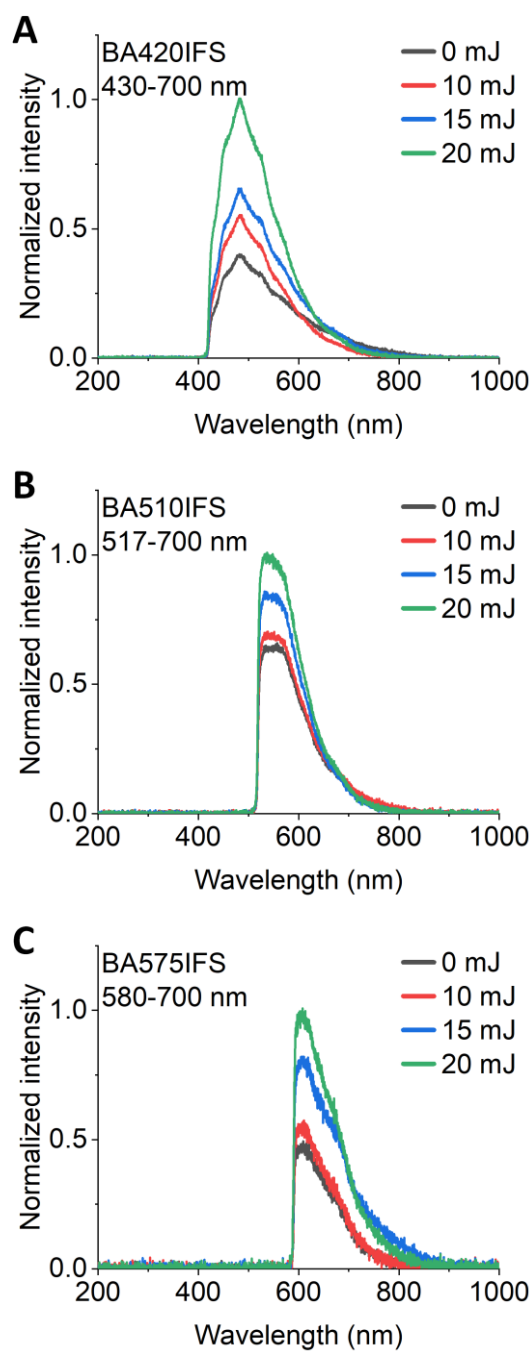
Supplementary fig 32. Bright-field optical microscopy images of microstructures patterned in PEGDA-based photo-polymer thin films using the dynamic scanning laser writing system. The images demonstrate large-area pattern formation and confirm successful optical readout using the wide-field imaging configuration.



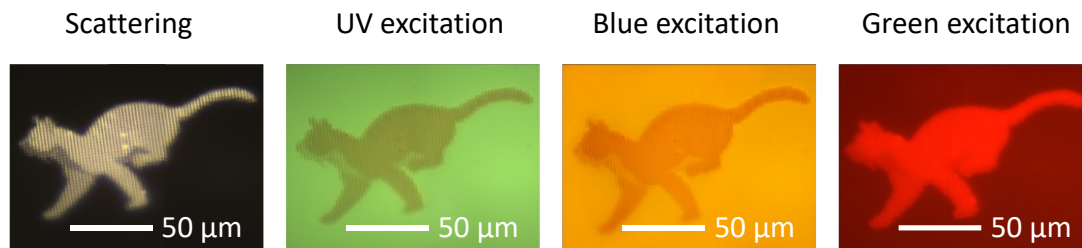
Supplementary fig 33. Wide-field UCPL images of patterns fabricated using a coupled dynamic scanning laser writing system in PEGDA-based photo-polymer thin films. Optical readout was performed using wide-field UCPL detection with different microscope objectives, including (A) a 100 $\times$ objective and (B) a 40 $\times$ objective.



Supplementary fig 34. Running cat pattern written by GS-assisted large-area laser writing. Bright-field optical microscopy images of a running cat pattern fabricated within PEGDA-based photo-polymer thin films using GS-assisted large-area fs-laser scanning. The images demonstrate the capability of dynamic scanning for writing extended optical patterns suitable for wide-field readout.

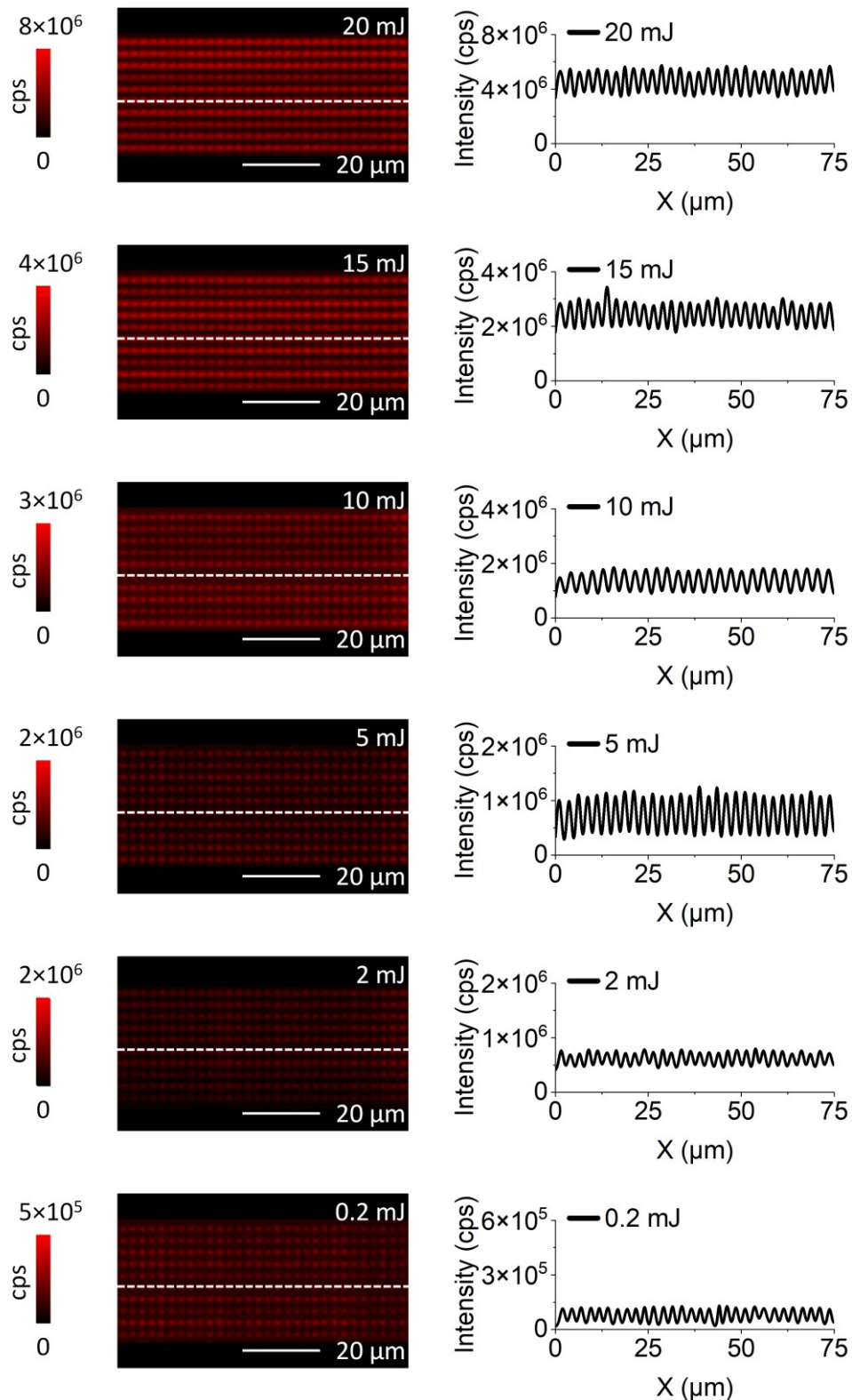


Supplementary fig 35. DCF emission spectra. Emission spectra of the DCF fluorescent dye measured under (A) UV, (B) blue, and (C) green excitation wavelengths. The spectra illustrate the excitation-dependent fluorescence response of DCF used for wide-field fluorescence imaging experiments.

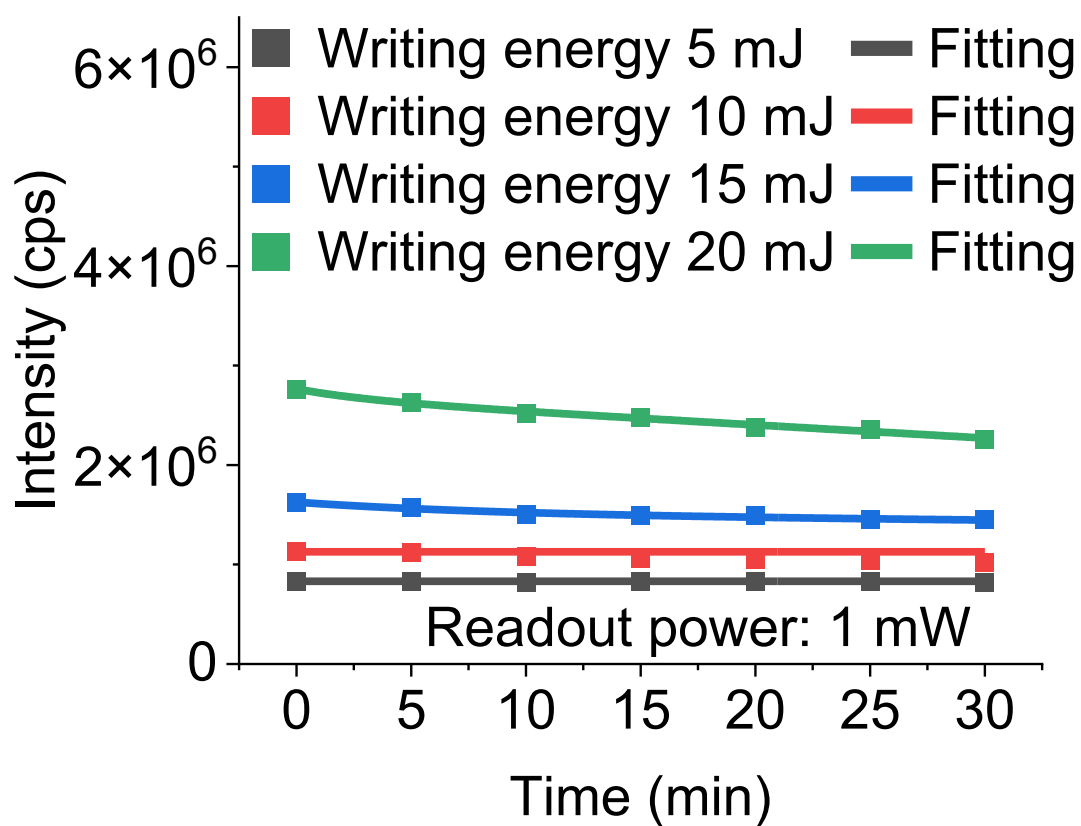


Supplementary fig 36. Wide-field fluorescence images of optical patterns detected through DCF emission. Fluorescence images were recorded using microscope objectives with magnifications of 100 $\times$, demonstrating the capability of the imaging system to resolve patterned structures at different spatial scales.

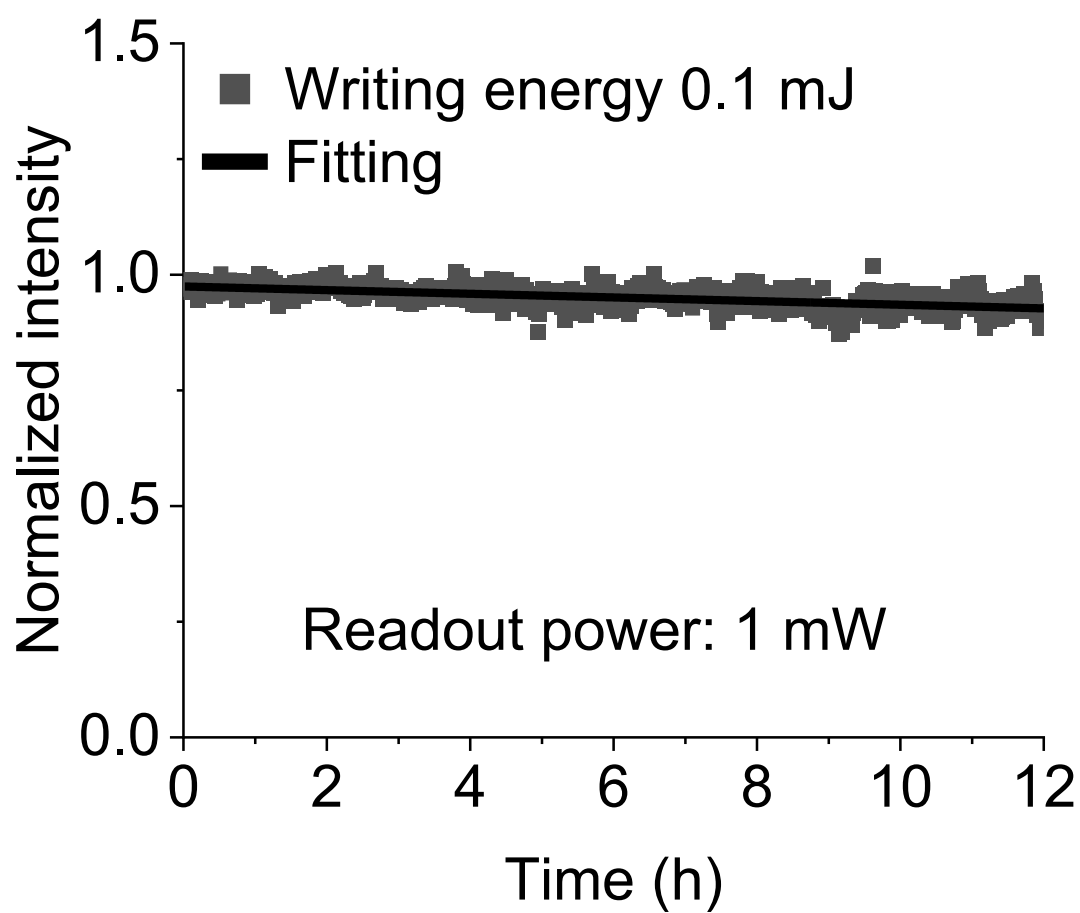
VII. Performance Metrics and Reliability



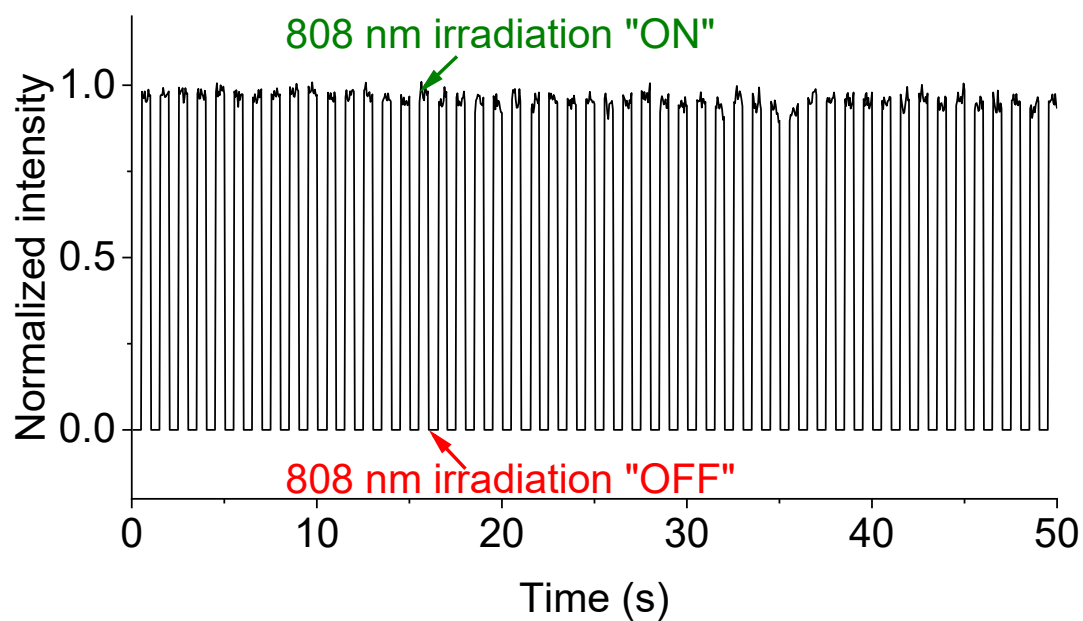
Supplementary fig 37. Writing cyclability of optical data bits. UCPL intensity of individual PEGDA-based photo-polymer dots was measured over 300 consecutive fs-laser writing cycles at various energies, demonstrating stable, reproducible signals for each dot.



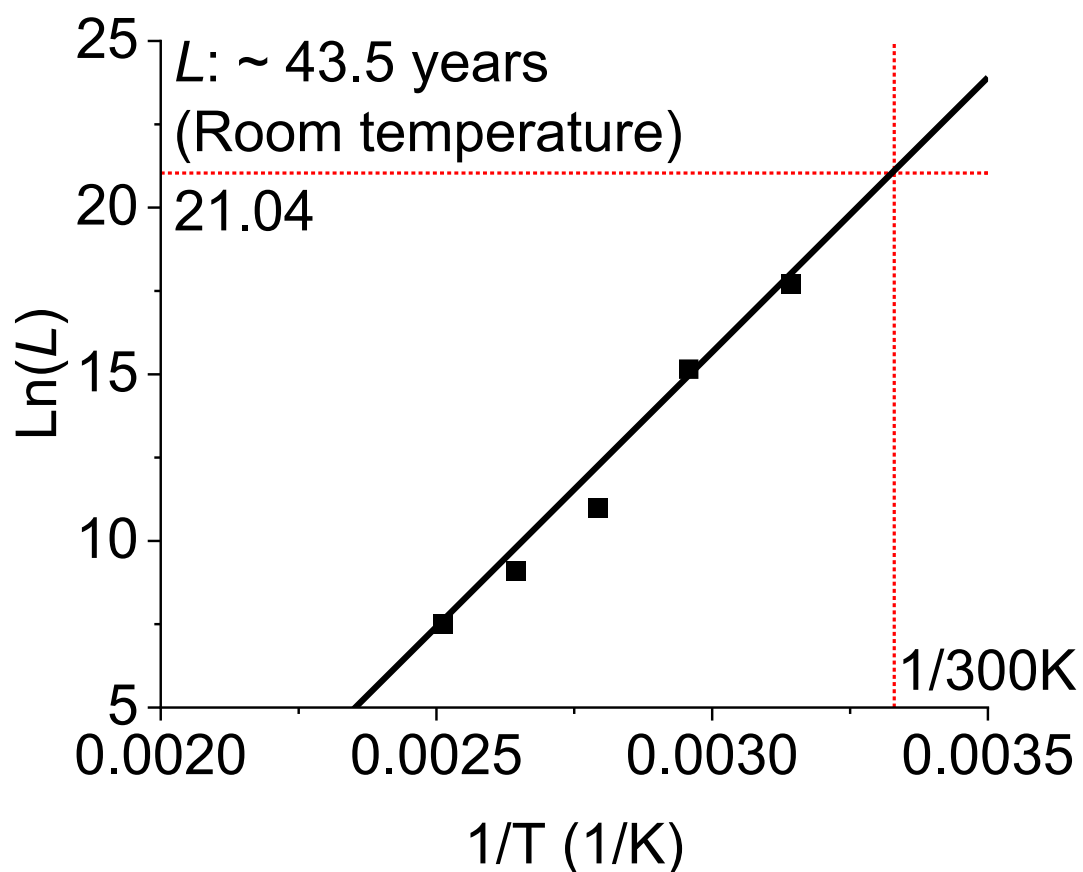
Supplementary fig 38. Energy-dose-dependent UCPL intensity. UCPL intensity from fs-laser-written structures measured at different energy doses, showing stable emission with minimal reduction over time and identifying optimal writing conditions.



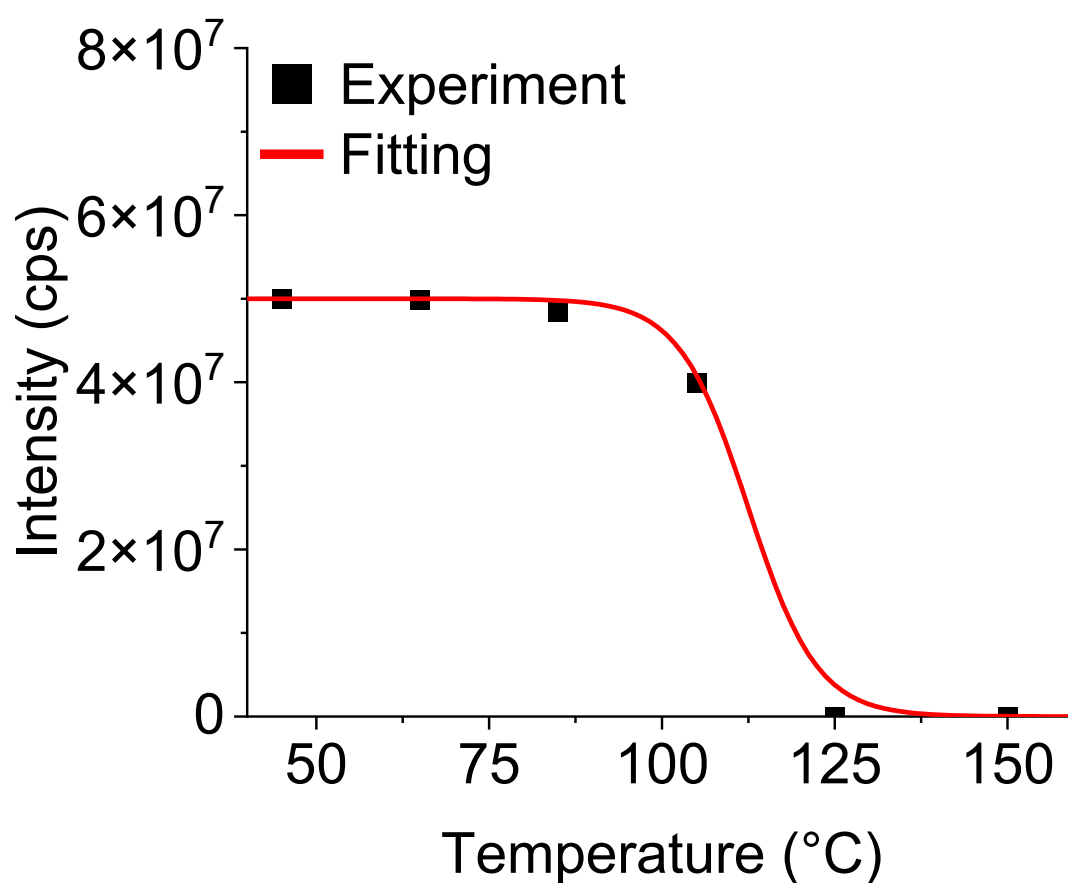
Supplementary fig 39. Continuous readout stability. UCPL intensity monitored during continuous optical readout under 808 nm excitation over a period of 12 hours. The results demonstrate the stability of UCPL emission during prolonged illumination, indicating the robustness of the laser-written structures.



Supplementary fig 40. Readout cyclability test. UCPL intensity measured during 50 repeated ON/OFF optical readout cycles under 808 nm excitation. The measurements confirm the reproducibility and stability of UCPL signals during repeated readout operations in PEGDA-based photo-polymer optical storage films.



Supplementary fig 41. Accelerated aging and lifetime estimation. Arrhenius analysis of UCPL signal retention measured under elevated temperature conditions. Accelerated aging experiments were performed to estimate the long-term stability and projected lifetime of optical data stored in PEGDA-based photo-polymer thin films.



Supplementary fig 42. Temperature-dependent UCPL stability. UCPL intensity measured after heating PEGDA-based photo-polymer thin films at different temperatures, demonstrating the thermal stability of the laser-written structures and the robustness of UCPL emission under elevated temperature conditions.

Supplementary Tables

Table S1. Key experimental parameters for static and dynamic laser writing and readout systems. Comparison of laser sources, excitation geometries, scanning configurations, optical components, and operating conditions used for static writing, time-response writing, dynamic writing, and static and dynamic readout experiments.

Parameter	Writing			Readout	
	Static	Time-response	Dynamic	Static	Dynamic
Laser source	Pulsed laser	Pulsed laser	Pulsed laser	CW laser	CW laser
Wavelength	460 nm	460 nm	460 nm	808 nm	808 nm
Repetition rate	80 MHz	100 Hz	80 MHz	CW	CW
Pulse width	<150 fs	<205 fs	<150 fs	—	—
Detector	—	—	—	SPAD	EMCCD (Andor iXon Ultra 888)
Objective	100×, NA = 1.5, oil immersion	100×, NA = 1.5, oil immersion	100×, NA = 1.5, oil immersion	100×, NA = 1.5, oil immersion	100×, NA = 1.5, oil immersion
Excitation geometry / scan mode	Focused point-by-point (sample scanning)	Focused point-by-point (sample scanning)	Focused galvo scanning (beam scanning)	Focused point-by-point (sample scanning)	Wide-field line scanning (beam scanning)
Scanner	Piezo stage (sample translation)	Piezo stage (sample translation)	2D galvo mirrors	Piezo stage (sample translation)	1D galvo mirror
Scanning speed / frequency	—	—	33.3 m s ⁻¹	—	5.8 kHz
Lateral spacing	1 μm	1 μm	2 μm	1 μm	2 μm
Axial spacing	5 μm	5 μm	10 μm	5 μm	10 μm
Laser power	10 mW	0.15 μW	20 mW	1 mW	100 mW
Modulation / acquisition control	Mechanical shutter	Mechanical shutter	Acousto-optic modulator (AOM)	Mechanical shutter	EMCCD frame rate
Exposure time	10 ms	10 ms	160 ns	10 ms	1 μs
Pulse number	8 × 10 ⁵	1	≈13	CW	CW

Table S2. Elemental composition of PEGDA-based photo-polymer thin films without and with photo-initiator before and after fs-laser writing. The elemental composition was analyzed by XPS to evaluate chemical changes associated with laser-induced photo-carbonization.

	C1s (%)	O1s (%)	C-C/C=C (%)	C-O (%)	C=O (%)
Without PI before laser writing	32.55	23.07	1.83	23.84	18.67
Without PI after laser writing	42.73	17.83	1.54	15.88	22.03
With PI before laser writing	44.33	14.97	5.01	26.82	28.88
With PI after laser writing	44.72	14.07	5.07	26.69	29.44

Table S3. UCPL lifetime distribution measured across multiple spatial positions. Statistical distribution of UCPL lifetimes measured at 14 independent spatial positions within regions written by the 460 nm fs laser in PEGDA-based photo-polymer thin films. The data demonstrate the spatial uniformity, reproducibility, and stability of UCPL emission across the patterned structures.

Position	UCPL lifetime (μ s)	Position	UCPL lifetime (μ s)
1	1.88	8	1.63
2	1.99	9	1.56
3	1.40	10	1.77
4	2.02	11	1.79
5	1.66	12	1.94
6	2.00	13	1.27
7	1.70	14	1.64

Table S4. Comparison of key parameters of representative high-capacity ODS and encoding technologies. The table summarizes representative approaches based on super-resolution and intensity-multiplexing ODS, highlighting differences in materials, writing and readout mechanisms, achievable grayscale levels, layer numbers, and resulting storage capacities.

Metric	Silica (Nature 2026) [4]	UCNP RETA (Sci. Adv. 2021) [5]	AIE-DDPR Disk (Nature 2024) [6]	Diamond (Nat. Photon. 2024) [7]	Current Work
Medium	Fused / borosilicate glass	Upconversion nanoparticles (UCNPs) + graphene oxide	Aggregation-induced emission dye-doped photo-polymer (AIE-DDPR)	Diamond with optically active defects	PEGDA / photo-polymer
Writing mechanism	Fs laser voxels (phase & birefringent encoding)	Upconversion RETA dual-beam CW writing + deactivation	Dual-beam fs writing + CW deactivation	Fs laser defect writing	Confocal & GS fs writing of u-CPDs
Readout method	Wide-field microscopy + machine learning	Super-resolution STED / confocal imaging	Super-resolution STED / confocal imaging	Confocal or wide-field fluorescence	Confocal or wide-field UCPL
Encoding	3D multi-level voxels (amplitude, phase, azimuth)	Nanoscale bit demonstration	3D binary multilayer (100 layers)	3D multi-level defect states	3D multi-level grayscale
Minimum voxel / pitch	$\sim 500 \times 485$ nm	~ 50 nm	~ 54 nm lateral, ~ 70 nm pitch	~ 200 nm	~ 500 nm
Layer spacing & # of layers	~ 6 μ m & 301 layers	Not specified (proof-of-concept)	1 μ m & 100 layers	~ 0.3 μ m & >300 layers	3–7 μ m & ~ 200 –300
Density / Capacity	1.59 Gbit/mm ³ (~ 4.84 TB)	Demonstration of nanoscale bits	1.6 Pbit per DVD-sized disk	~ 14.8 Tbit/cm ³	0.4 Pbit per DVD-sized disk
Write throughput	25.6–65.9 Mbit/s	Not quantified	Prototype scanning only	$\sim$ Mbit/s scale	~ 10 –50 Mbit/s
Lifetime / Stability	$>10,000$ yrs (accelerated testing)	Not quantified	~ 41 yrs estimate	Extremely long (diamond defects)	~ 43.5 yrs estimate

Supplementary References

1. Levin, M., Tang, Y., Eisenbach, C., Valentine, M. & Cohen, N. Understanding the response of poly(ethylene glycol) diacrylate (PEGDA) hydrogel networks: a statistical mechanics-based framework. *Macromolecules* **57**, 7074–7086 (2024).
2. Loh, K. P., Bao, Q., Eda, G. & Chhowalla, M. Graphene oxide as a chemically tunable platform for optical applications. *Nat. Chem.* **2**, 1015–1024 (2010).
3. Crochet, J., Duque, J. G., Werner, J. H. & Doorn, S. K. Photoluminescence imaging of electronic-impurity-induced exciton quenching in single-walled carbon nanotubes. *Nat. Nanotechnol.* **7**, 126–132 (2012).
4. Microsoft Research Project Silica Team. Laser writing in glass for dense, fast and efficient archival data storage. *Nature* **650**, 606–612 (2026).
5. Lamon, S., Wu, Y., Zhang, Q., Liu, X. & Gu, M. Nanoscale optical writing through upconversion resonance energy transfer. *Sci. Adv.* **7**, eabe2209 (2021).
6. Zhao, M. *et al.* A 3D nanoscale optical disk memory with petabit capacity. *Nature* **626**, 772–778 (2024).
7. Zhou, J. *et al.* Terabit-scale high-fidelity diamond data storage. *Nat. Photonics* **18**, 1327–1334 (2024).