




Two-step absorption instead of two-photon absorption in 3D nanoprinting

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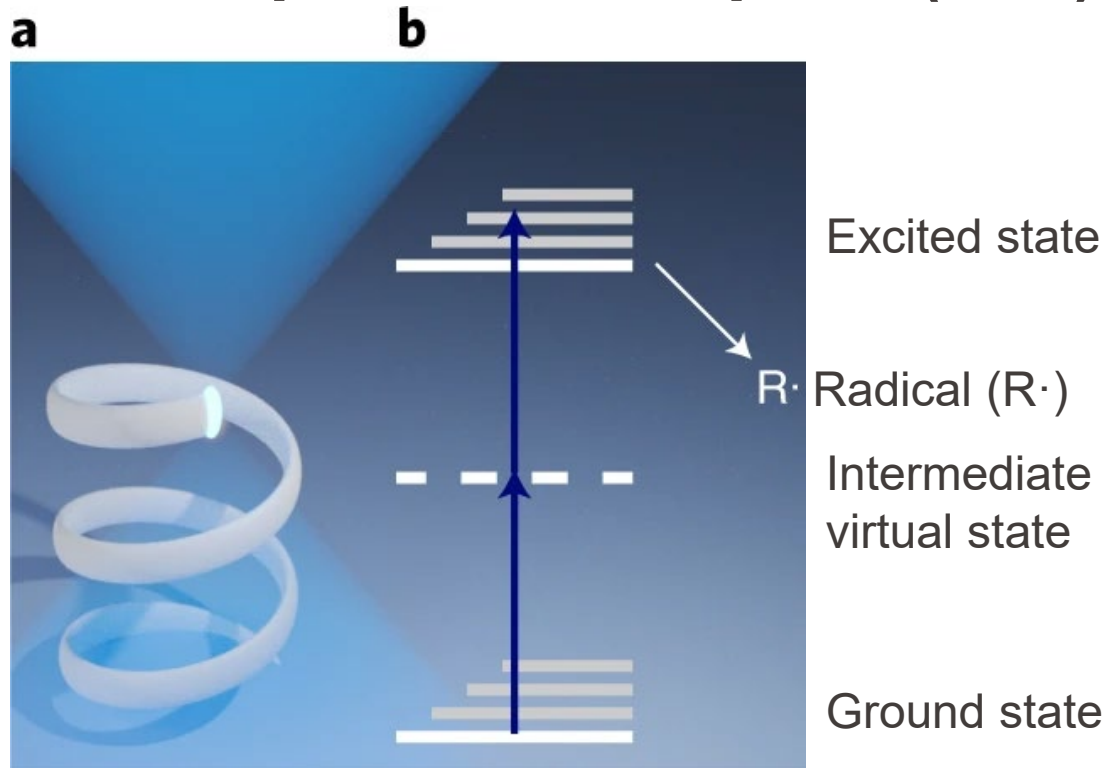
Two-step absorption instead of two-photon absorption in 3D nanoprinting

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Optical nonlinearity  **Crucial spatial concentration of optical excitation in 3D laser printing**



1. Photoinitiator transition rate \propto light intensity squared (I^2)

2. Exposure dose (D) $\propto I^2$

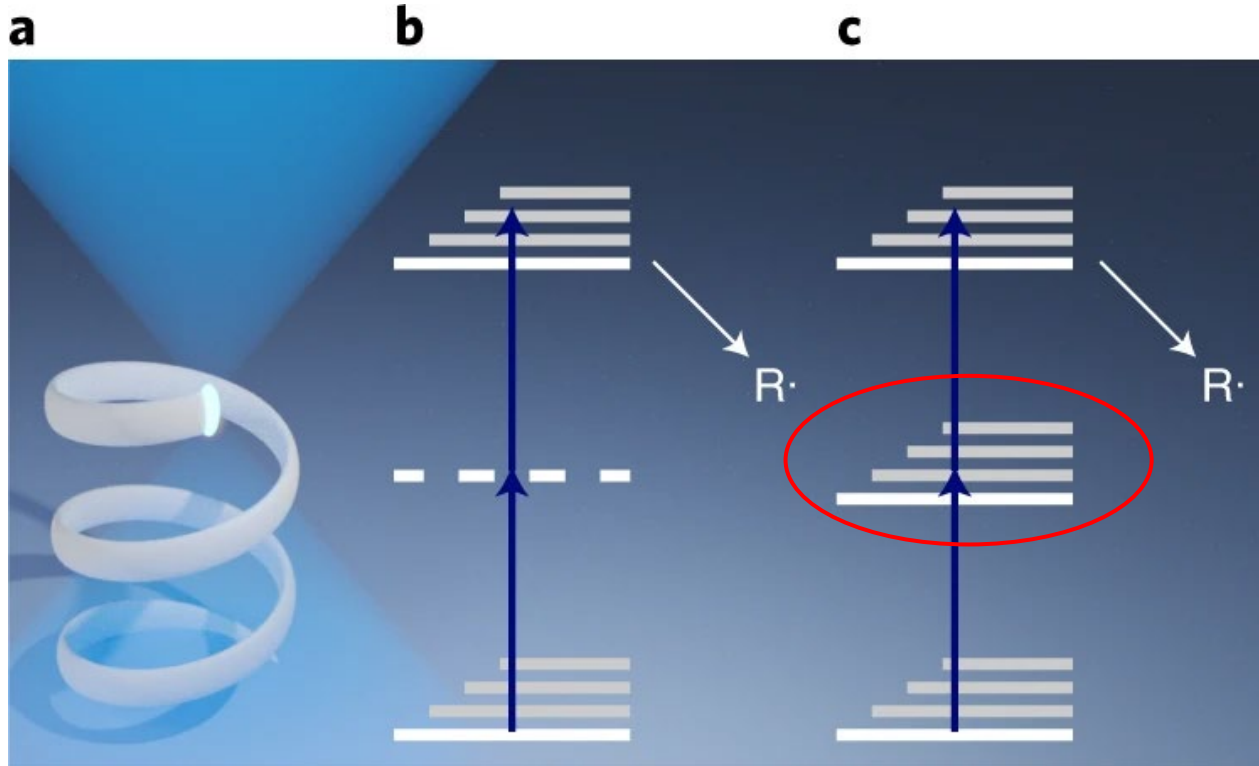
Light intensity \longrightarrow Accuracy

This quadratic nonlinearity suppresses unavoidable lateral and axial tails of the diffraction-limited laser focus, warrants the crucial concentration of the excitation and the chemical reaction along all three spatial directions.

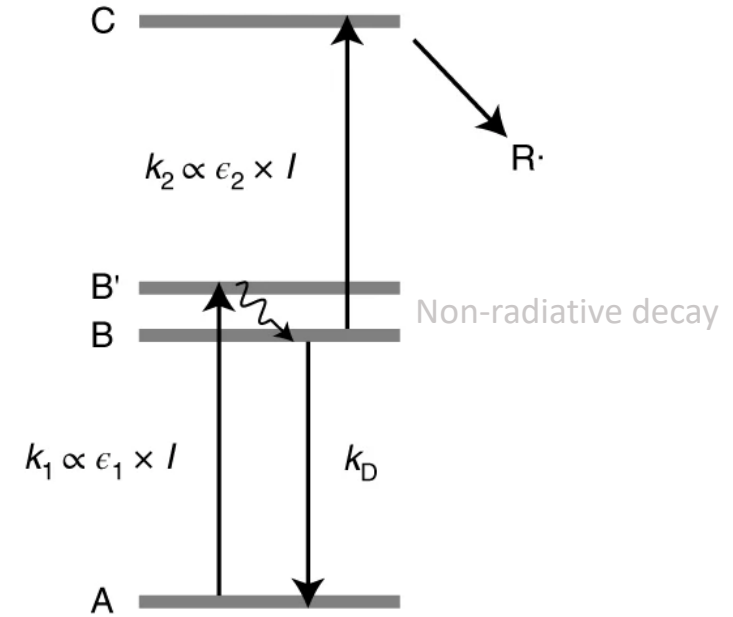
Light intensity $\longrightarrow ? \longrightarrow$ Safety

To obtain efficient two-photon absorption, mode-locked pico- or femtosecond laser sources are routinely used.

$I = 10^{12} \text{ W cm}^{-2}$ Micro-explosions, unwanted population of high-energy electron states. Expensive.



An intermediate electronic state that exists without the light field.



Simplified energy-level model and rate-equation calculations for a TSA photoinitiator.

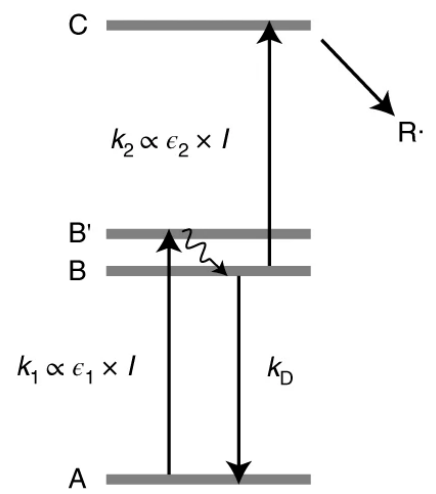
1. The ratio of the real-state lifetime to the virtual-state lifetime increased.

EPFL Two-step Absorption (TSA)

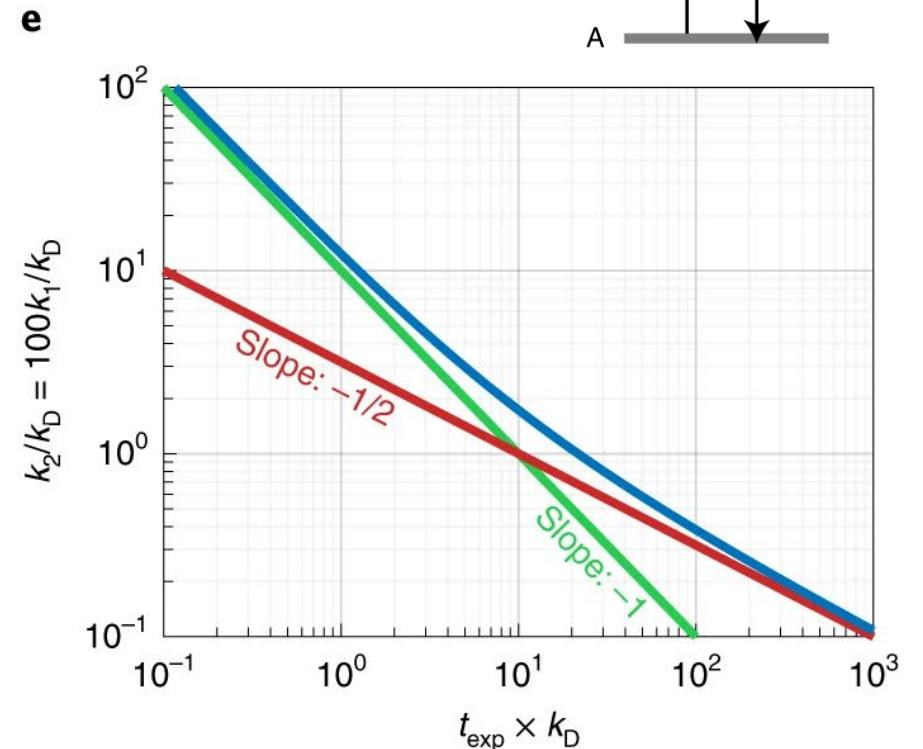
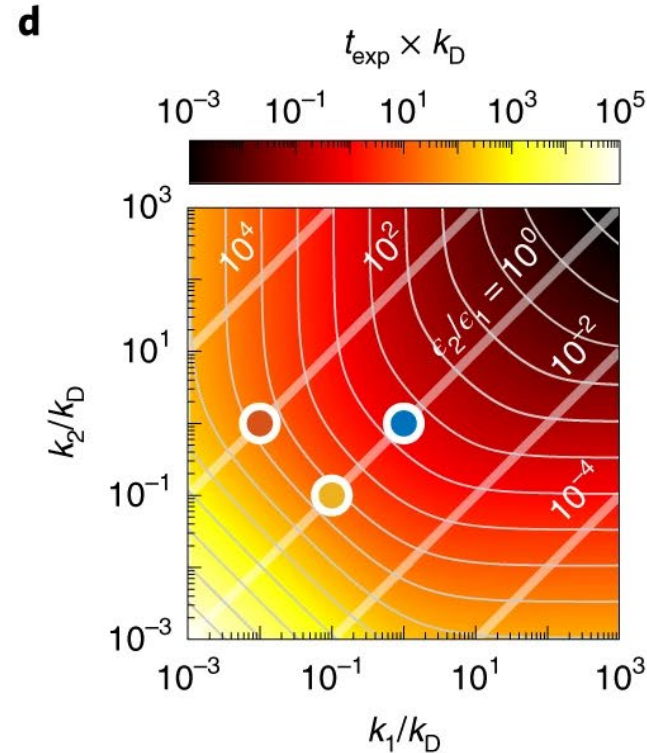
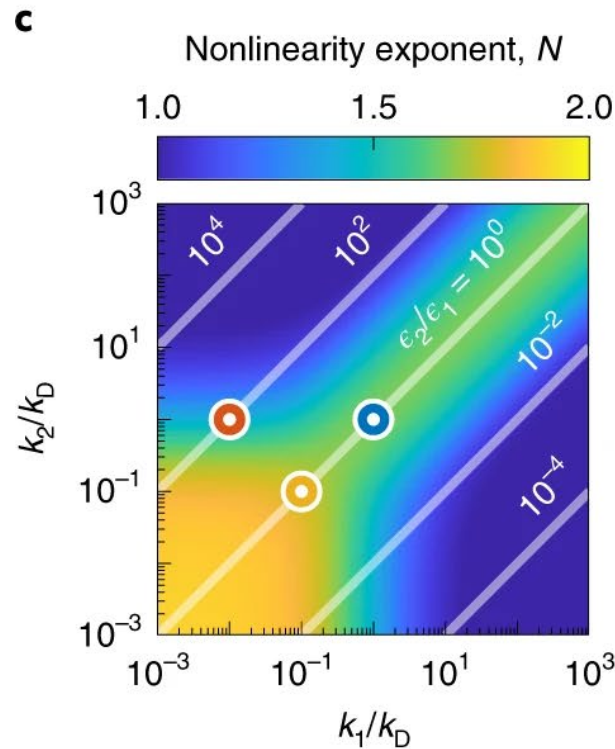
1. The ratio of the real-state lifetime to the virtual-state lifetime increased.

2. $D \propto I^2$ Capable of achieving high-resolution 3D aggregation

$D=0.1$



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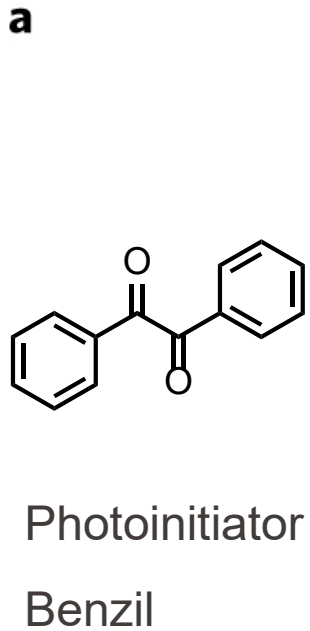
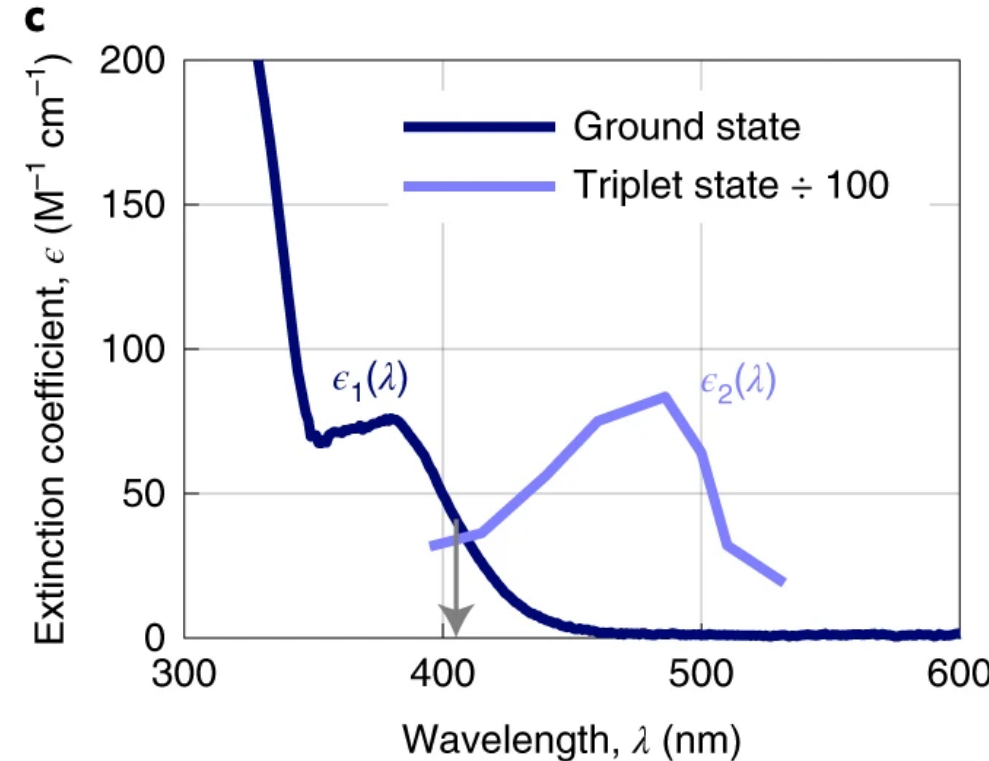
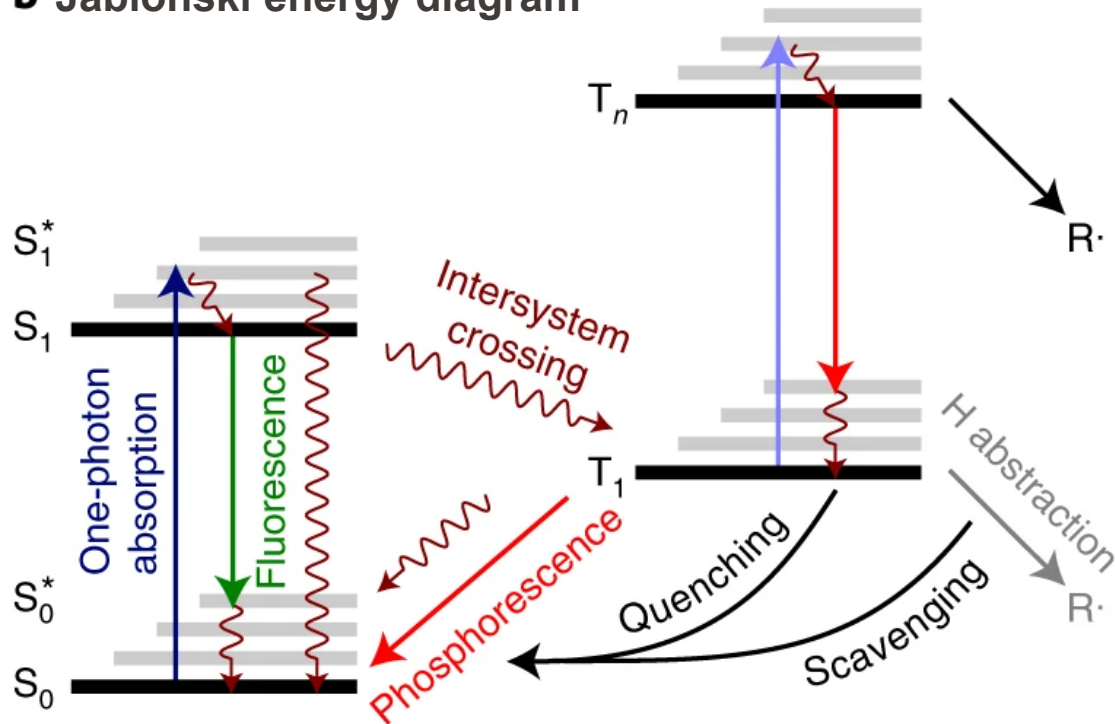


Left $D \propto t^2 I^2$
 $D=0.1$
 $I \propto t^{-1/2}$

Right $D \propto t I^2$
 $D=0.1$
 $I \propto t^{-1}$

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Blue $N = 1$ single photon absorption
 Yellow $N = 2$ Second-order nonlinearity
 Green k_1, k_2 (rate coefficients) large, $D \propto I^2$

**b** Jablonski energy diagram

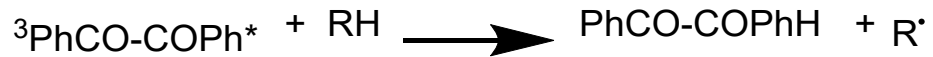
Real intermediate states: S_1 and T_1 . $S_0 \xrightarrow{h\nu} S_1 + T_1$

Second photon excites to $T_n \rightarrow$ radical formation \rightarrow polymerization

The ground-state extinction is about 100 times lower than triplet-state extinction, resulting in over typical free-working distances of microscope objective lenses. Due to the relatively high transient extinction, even moderate intensities are sufficient to promote a considerable fraction of triplet-excited molecules to a higher-excited triplet state.

1. The ratio of the real-state lifetime to the virtual-state lifetime increased.
2. $D \propto I^2$ Capable of achieving high-resolution 3D aggregation
3. An electron in the intermediate state may already trigger a polymerization reaction

Triple-state hydrogen abstraction side reaction



TEMPO/BTPOS scavenger suppresses unwanted one-photon reaction

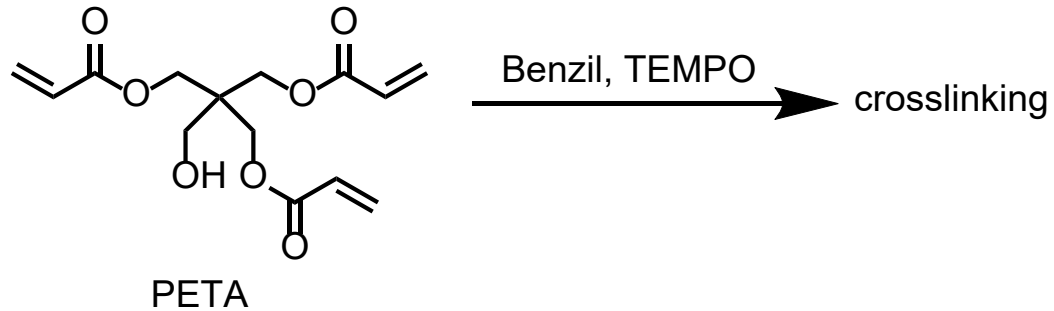
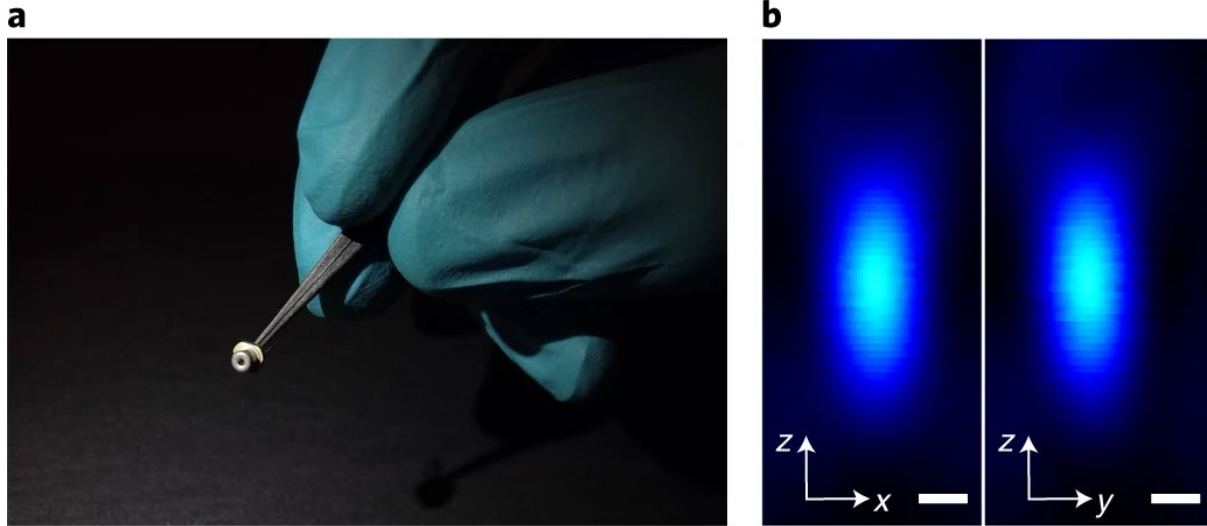
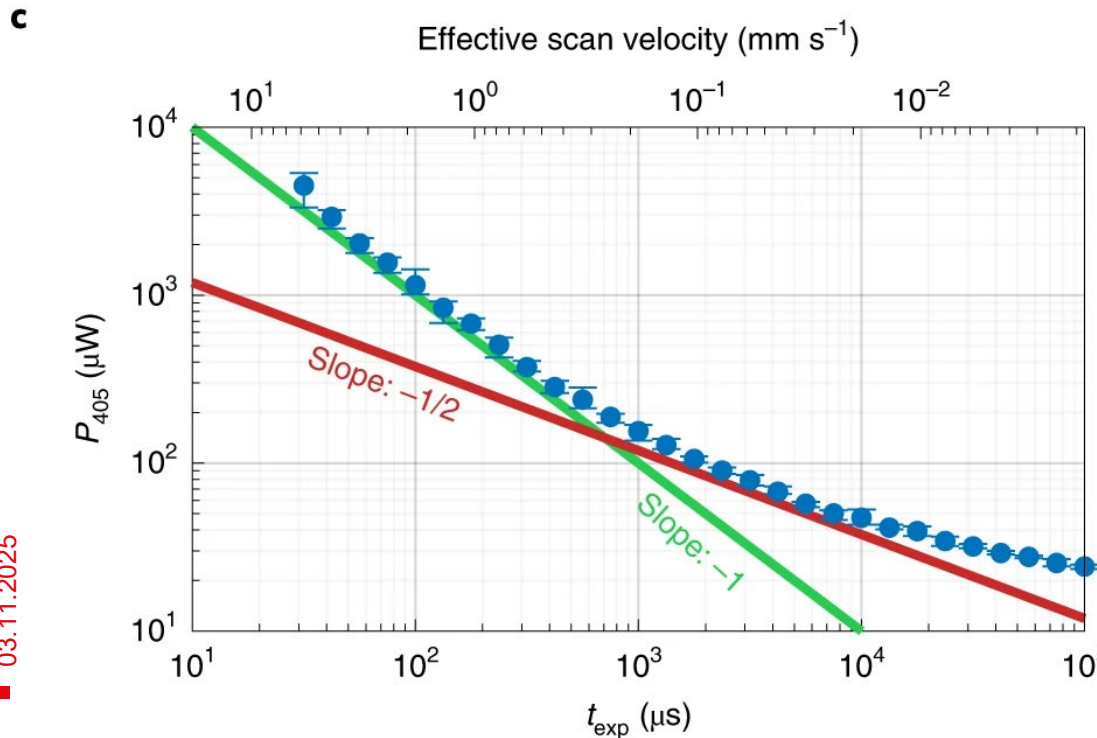


Fig. S9 | Photograph of the used microscope objective lens with applied photoresist for dip-in 3D laser nanoprinting. For dip-in 3D laser nanoprinting, the amount of applied photoresist is on the order of a few microliters. Therefore, the photoresist cannot be seen on this photograph. Note that the bronze colored disk on top of the microscope lens is not the photoresist, but part of the objective lens metallic body.



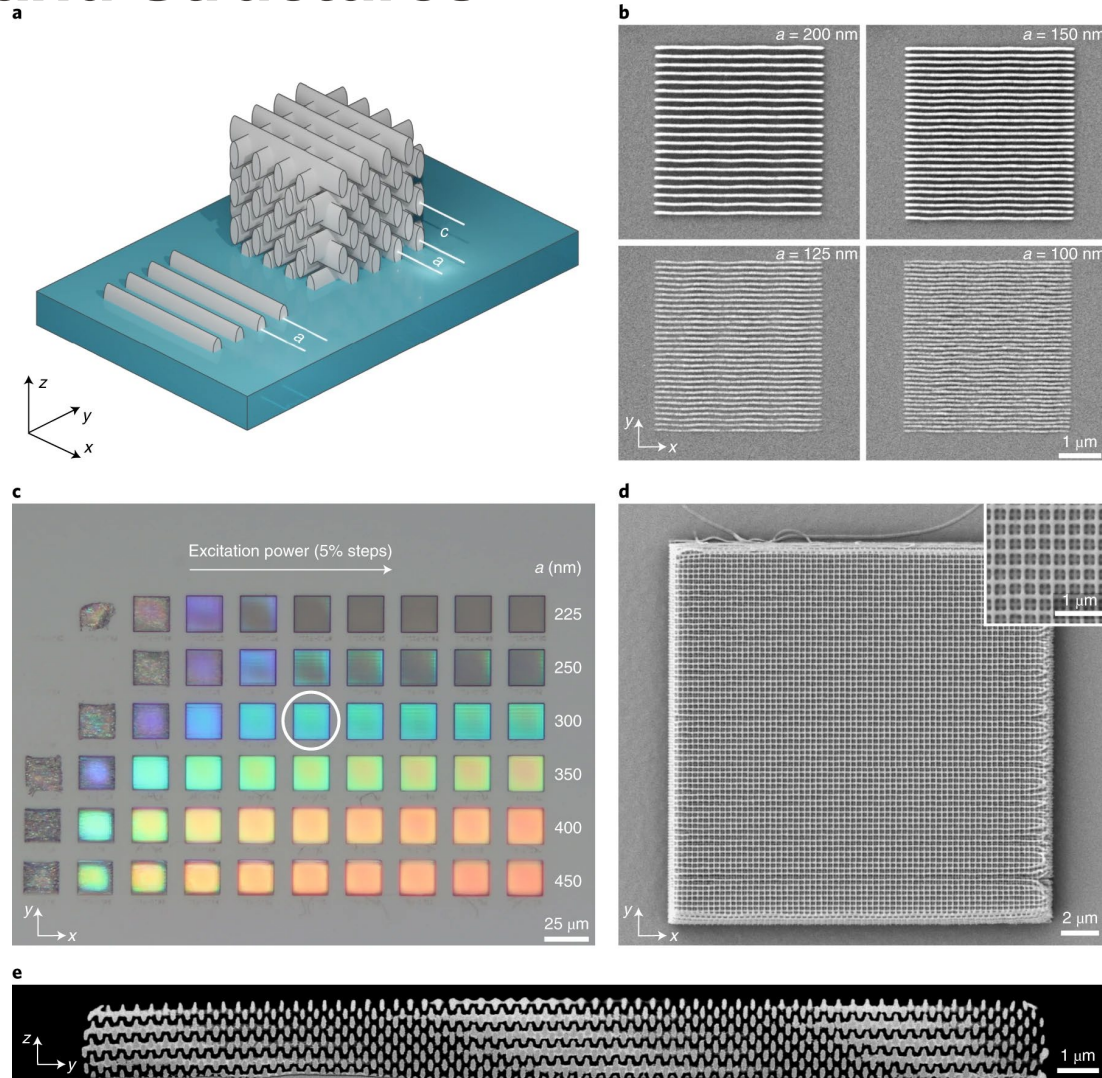
The aspect ratio of 2.5 of the axial and lateral-intensity FWHM indicates a diffraction-limited laser focus.



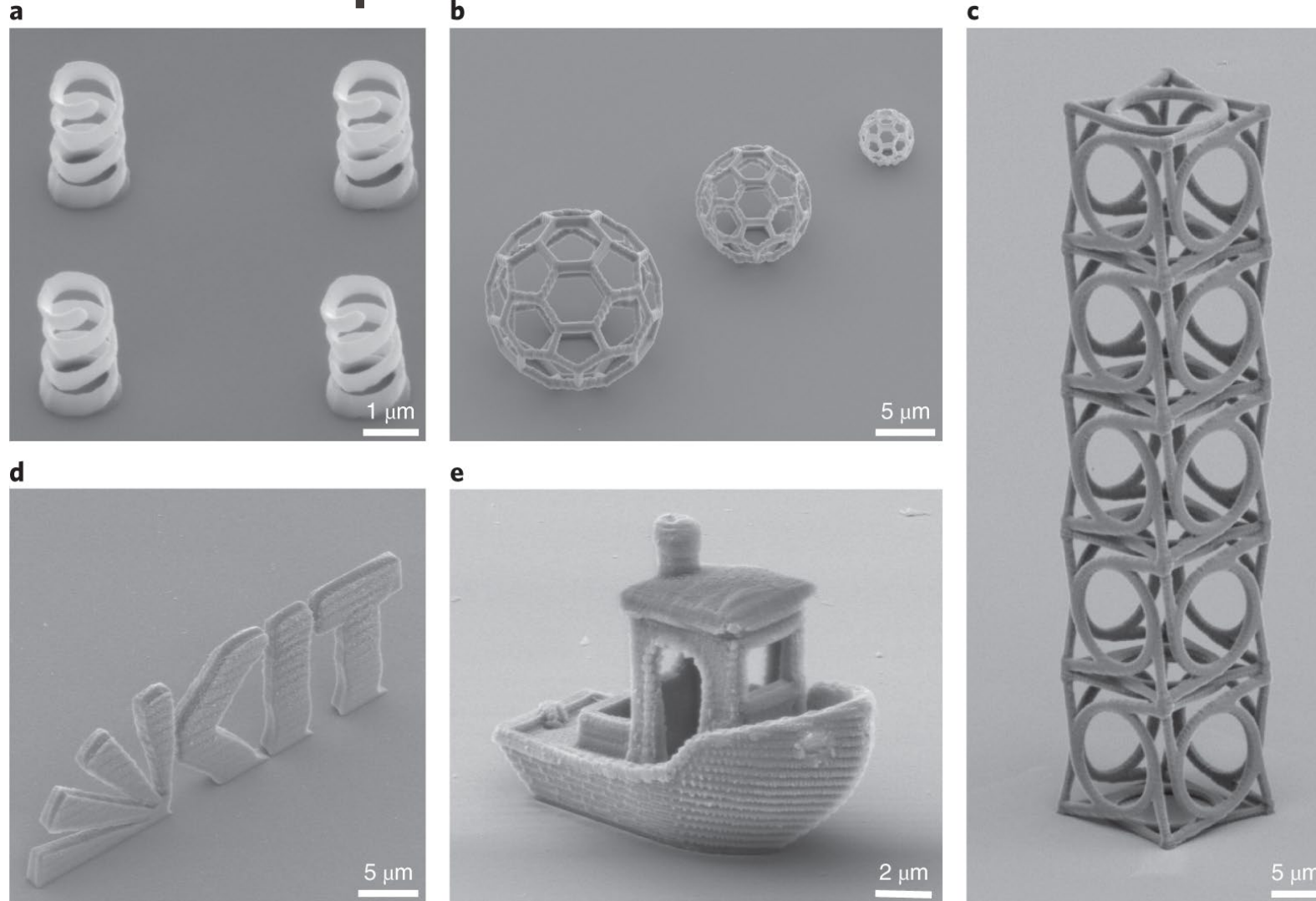
405 nm CW diode laser ($\sim 45\text{--}100 \mu\text{W}$)

Focus characterized by gold nanoparticle scanning

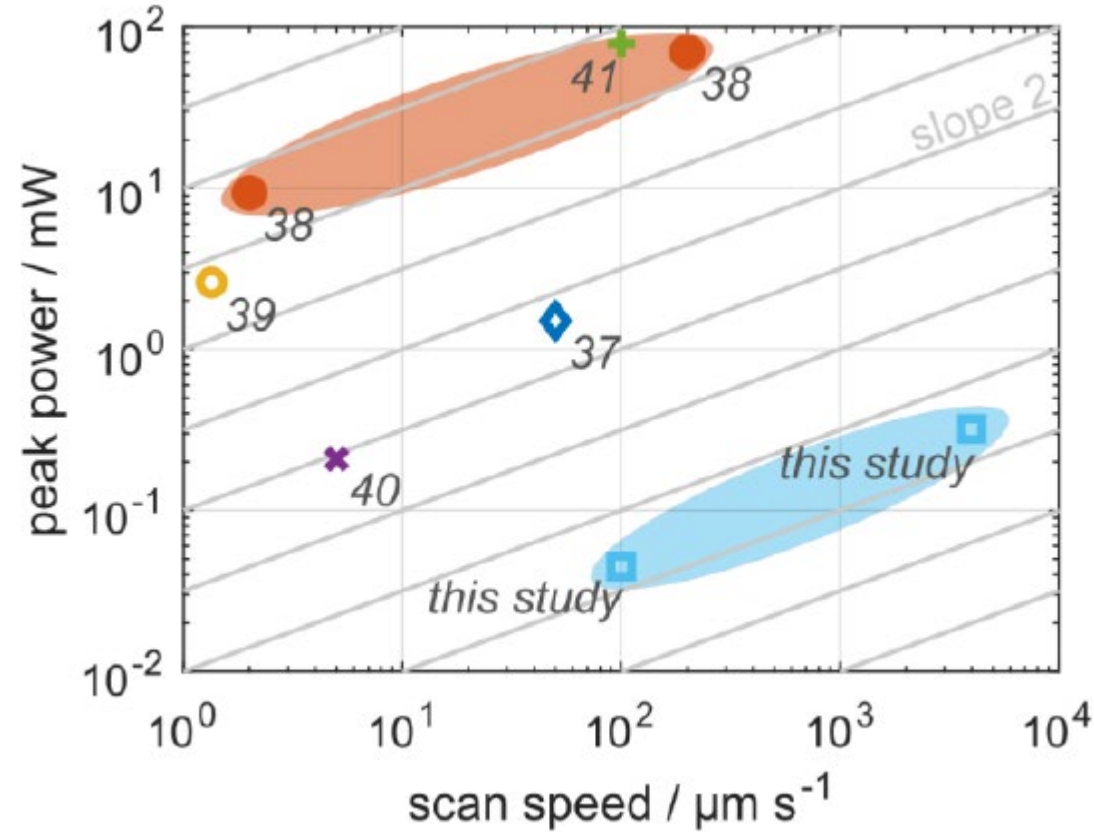
Exposure time vs power measurements confirm TSA behavior



1. Dense periodic line gratings: < 150 nm period, Surpass STED-based multiphoton 3D 800 nm
2. 3D woodpile photonic crystals: 24 layers, no proximity effects
3. Same spatial resolution as STED-enhanced TPA



1. Complex structures: helices, buckyballs, KIT logo, 3D Benchy
2. Demonstrates stable printing and high fidelity
3. Works in “dip-in” mode with matched refractive index



Advantages of Two-step Absorption

TSA = new nonlinear excitation mechanism for 3D nanoprinting

Quadratic dependence (I^2) confirmed both theoretically and experimentally

Enables compact, affordable, reliable nanoprinting systems

Potential for integration with STED and dual-color printing



Thank you!

Suqiu Jiang

3rd November 2025