Supporting Information

3D printed Complex Microstructures with Self-sacrificial Structure

Enabled by Grayscale Polymerization and Ultrasonic Treatment

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Section S1. The detailed parameters of 3D printing system.

The UV light energy is determined by the different setting values of the 3D printer corresponding to the different needed light intensity ($I_0$) for a white digital mask with different layer thicknesses. The $I_0$ was measured by a standard photodiode power sensor (THORLABS S120VC). The length and width of the tested digital mask are 2 mm. The sensor was precisely adjusted to be placed at the focal position of the DMD mirrors. After the digital mask was projected onto the sensor, the power of the digital mask on the LCD panel (PM100D) was obtained. Then, the UV light intensity ($I_0$) can be calculated by

$$I_0 = \frac{P}{S} \quad (1)$$

where $P$ is the measured power and $S$ is the area of the digital mask. It can be seen from Figure S1(A) that the corresponding $I_0$ for a digital mask ranges from 100 mW/cm² to 1100 mW/cm² with the setting value of the 3D printer ranges from 0 to 255, and the $I_0$ increases with the increase of the setting value. The $I_0$ sharply raises with the setting value in the range of 0 to 50, but the increasing rate decreases with the increase of the setting value afterwards. It was found that the digital mask was distorted with a setting value (on behalf of UV light intensity) larger than 40 during the test. Therefore, the light intensity was set as 40 to promise the speed of the manufacturing as a constant. Besides, the grayscale value of the digital mask also ranges from 0 to 255, which represents the brightness of the digital mask being pure black (grayscale value of 0) to pure white (grayscale value of 255). It can be observed from Figure S1(B) that the light intensity of the digital mask increases with the increase of the grayscale value. The $I_0$ for a white digital mask (grayscale value is set to 255) was 525 mW/cm².
**Figure S1** The detailed parameters of the PμSL based 3D printing technique. (A) The UV light intensity as a function of the printer’s setting value. (B) The UV light intensity as a function of the grayscale value.
Section S2. The composition of the resin and its penetration depth.

The generation of radicals follows the excitation of initiators by the incident photons from the illuminated UV light. Then, the radicals react with the monomer molecules to form big molecules. Those big molecules form a stable polymer chain after their approach, and those stable polymer chains finally form the solidified polymer structures (Figure S2(A)). Meanwhile, it should be noted that the absorption of UV light within UV-curable resins obeys the Beer-Lambert law. The UV light intensity $I(z)$ can be expressed by the following formula:

$$I(z) = I_0 e^{-z/D_p}$$  \hspace{1cm} (2)

where $I_0$ is the intensity at the resin surface calculated by Eq. 1, and $D_p$ is the transmission depth of light in the resin. As a result, the intensity of UV light decreases exponentially with the increase of transmission depth, which can be observed from Eq. 2. Then the curing depth of resin ($C_d$) can be expressed by the following formula:

$$C_d = D_p \ln \left( \frac{E_0}{E_c} \right)$$  \hspace{1cm} (3)

where $E_c$ is the critical does of curing exposure of resin, while the required light intensity at the resin surface for the solidification of the resin is $E_0 = I_0 t$, where $t$ is the exposure time illuminated by UV light. The curve of the curing depth versus light intensity can help the researchers to precisely control the complete solidification of the resin with different layer thicknesses, which is shown in Figure S2(B). Furthermore, the results can also help to increase the fabrication speed by precisely controlling the exposure time. In addition, it can be observed that the $D_p$ of the present resin is 57.5 $\mu$m and the $E_c$ equals to 550 $\text{mJ/cm}^2$. 

**Figure S2** The composition of the present resin and its penetration depth. (A) The composition of the present resin. (B) The curing depth as a function of the light dose.
Section S3. Theoretical study of ultrasonic cavitation and simulation analysis of its influencing factors.

The cavitation process is actually the motion process of cavitation bubble wall. When a beam of ultrasonic wave \((p_a \sin \omega_a t)\) propagates in the liquid, the tiny bubbles in the liquid will be stretched and compressed by the ultrasonic wave. Make the following assumptions for cavitation bubbles\(^1\):

1. Cavitation bubbles always maintain a spherical structure during the movement;
2. Assume that cavitation bubbles exist in an infinite liquid space;
3. The temperature and density of the surrounding liquid medium always remain unchanged;
4. Ignore the influence of gravity and buoyancy on cavitation bubbles;

The initial pressure inside \(p_{in}\) and outside \(p_{out}\) of the cavitation bubble with radius \(R_0\) are:

\[
p_{in} = p_g
\]

\[
p_{out} = p_0 + \frac{2\sigma}{R_0} + \frac{4\mu R}{R}
\]

where \(p_g\) is the pressure inside the bubble, \(p_0\) is the hydrostatic pressure, \(\sigma\) is the surface tension coefficient, \(\mu\) is the liquid viscosity, \(R\) is the instantaneous radius of the cavitation bubble and \(\dot{R}\) is the rate of change with time of the cavitation bubble. \(R\) can be expressed by the following formula\(^2-3\):

\[
R \left(\frac{d^2R}{dt^2}\right) + \frac{3}{2} \left(\frac{dR}{dt}\right)^2 = \frac{1}{\rho} (p_{in} - p_{out})
\]

The equation of motion of cavitation bubbles is obtained by substituting Eq. 4 and Eq. 5 into Eq. 6:

\[
R \dddot{R} + \frac{3}{2} \dot{R}^2 = \rho^{-1} \left[\left(p_0 + \frac{2\sigma}{R_0}\right) \left(\frac{R_0}{R}\right)^3 - \frac{2\sigma}{R} - \frac{4\mu\dot{R}}{R} - p_0 + p_{in} + p_a \sin \omega_a t\right]
\]
where, $\ddot{R}$ is the movement acceleration of the particle on the cavitation bubble wall, $p_a$ is the ultrasound sound pressure amplitude, $\kappa$ is the polytropic exponent of gas, $\rho$ is the density of gas in bubble and $\omega_a$ is the angular frequency of ultrasound.

The total kinetic energy of gas in bubble can be obtained by the following formula:\(^4\):

$$K = \frac{1}{2} (\frac{\ddot{R}}{R})^2 \int_0^R \rho r^2 4\pi r^2 dr = \frac{2}{5} \rho R^3 \ddot{R}^2$$ \hspace{1cm} (8)

where, $r$ is the distance between a gas molecule and the bubble center. At the time the cavitation bubble collapses, the value of the shock wave $p$ can be expressed by the following formula:\(^5\):

$$p = P_0 + \frac{\ddot{R}_{min}}{3r} \left[ \frac{3\gamma - 4}{\gamma - 1} R^3 \frac{P_{g1}}{a} + \frac{R^3 P_{g1}}{a} (R^3 - 4) P_0 + 3(\frac{\sigma}{R_0} + \frac{2\mu \ddot{R}}{R_0})(R^3 - 3R') \right] -$$

$$\frac{R_{min}^4}{3r^4} [(R^3 - 1) P_0 - \frac{P_{g1}}{a} (R^3 - R^3) + 3(\frac{\sigma}{R_0} + \frac{2\mu \ddot{R}_{min}}{R_0})(R^3 - R')]$$ \hspace{1cm} (9)

$$= P_0 + a \frac{\ddot{R}_{min}}{3r} - b \frac{R_{min}^4}{3r^4}$$

where, $R_{min}$ and $R_{max}$ are the minimum and maximum radius of cavitation bubbles, $R = \frac{R_{max}}{R_{min}}$, $\ddot{R}_{min}$ is the acceleration of the cavitation bubble at the minimum radius, $P_{g1}$ is the pressure inside the bubble at the maximum radius of the cavitation bubble, $\gamma$ is the adiabatic index, $a$ and $b$ are the values in the brackets.
Figure S3 The effect of amplitude of sound pressure ($p_a$) on the cavitation process. (A) The varied range of max bubble radius increases with the increase of the $p_a$. (B) The changed range of the $p_{out}$ increases with the increase of the $p_a$. 
Section S4. The stress distribution within the supporting structures with different grayscale value and diameter.

A  

[Stress distribution images with MPa values shown]

B  

[Stress distribution images with MPa values shown]

**Figure S4** The underlying mechanisms for the removal of the supporting structures affected by the grayscale. (A) The root of the supporting structure connects with the substrate. (B) The root of the supporting structure disconnects with the substrate. (i) Young’s modulus of material was set to 0.42 GPa, (ii) Young’s modulus of material was set to 1.14 GPa, (iii) Young’s modulus of material was set to 3.8 GPa. The diameter of the “street lamp” was 50 μm, the diameters of the supporting structure were 10 μm and 20 μm for the top and root of it, respectively, the height of the supporting structures was 160 μm.

The structures printed by PμSL system are also affected by the intensity of the UV light, which can be adjusted by the grayscale value of the DMD. The underlying mechanisms of supporting structures removal by adjusting the grayscale value of the
3D printing system are demonstrated in Figure S4. The diameter of the “street lamp” was 50 μm, the diameters of the supporting structure were 10 μm and 20 μm for the top and root of it, respectively, the height of the supporting structures was 160 μm. The grayscale values of the DMD are represented with the change of the Young’s modulus of material after 3D printing, which were set to 0.42 GPa, 1.14 GPa, and 3.8 GPa for the calculations in (i) to (iii) for both of Figures S4 (A) and S4 (B), respectively.

The calculated results for supporting structures with both two ends fixed are shown in Figures S4 (A). It can be seen from Figures S4 (A-i) to S4 (A-iii) that the maximum of the stress within the microstructures is the same. However, it should be noted that the places for the appearance of the maximum stress for the models with different Young’s modulus of material are totally different. Specifically, the maximum stress appears at the top of the supporting structure with Young’s modulus of material was set to 0.42 GPa, indicating that the connection between the top of the supporting structure and the “street lamp” breaks down first. In contrast, the maximum stress appears at the root of the supporting structure with Young’s modulus of material was set to 3.8 GPa. The calculated results for supporting structures with a free root are shown in Figures S4 (B). It can be observed from Figures S4 (B-i) to S4 (B-iii) that the maximum of the stress within the microstructures appears at the root of the supporting structures. In addition, the maximum stress within the supporting structure increases with the increase of the Young’s modulus of material, leading to a fact that it is much easier to remove a supporting structure printed with lower grayscale value of the DMD, which is consistent with the results demonstrated in Figure 2. The results clearly validate that the grayscale value of the DMD can be varied for the printing of the main structures and the supporting structures to optimize the removal of the supporting structures while the main structure will be well preserved with ultrasonic vibration.
**Figure S5** The underlying mechanisms for the removal of the supporting structures affected by the diameter. (A) Two ends were fixed. (B) The bottom was free. The diameter of the “street lamp” was 100 μm, the height of the supporting structures was 160 μm. The diameters of the supporting structure were 30 μm, 50 μm and 70 μm for (i)-(iii), respectively.

The effect of the diameter of the supporting structures is also numerically studied and the results are shown in **Figure S5**. The diameter of the “street lamp” was 100 μm, and the height of the supporting structure was 160 μm. The Young’s modulus of material was set to 3.8 GPa. The diameters of the supporting structure were 30 μm, 50 μm and 70 μm for **Figure S5** (i)-(iii), respectively. It can be seen from both of **Figures S5** (A) and S5 (B) that the maximum stress within the microstructures decreases with the increase of the diameter of the supporting structures, no matter both two ends are fixed or the root was free. It can be concluded that the supporting structures are harder to be removed with a larger diameter of them, which is similar to the results shown in **Figure 2**.
List of Movies:

**Movie S1 (.mp4 format).** The sound pressure distribution within the ethanol.

**Movie S1 (.mp4 format).** The stress distribution within the microstructures when both of two ends were fixed.

Reference

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