Multiphoton lithography based 3D micro/nano printing

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Multiphoton lithography

- Also known as direct laser lithography, direct laser writing or two-photon polymerisation
- Create arbitrary 3D nano/micro structures
- Based on NIF fs laser induced multi-photon polymerization
- Direct fabrication without a mask
- Materials: polymers, ceramics, metals, hybrid…
- Resolution: ~100 nm
# Micro-stereolithography vs. Multiphoton lithography

<table>
<thead>
<tr>
<th>Essential elements</th>
<th>CAD design, 2D layer preparation function, laser scanning &amp; controlling system with monitoring devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanism for polymerisation</td>
<td><strong>One-photon absorption</strong> (Linear absorption)</td>
</tr>
<tr>
<td>Laser type</td>
<td>UV laser</td>
</tr>
<tr>
<td>Resolution</td>
<td>~ 1 µm</td>
</tr>
<tr>
<td>Strategy for 3D fabrication</td>
<td>Polymerisation at the surface → layer-by-layer approach</td>
</tr>
</tbody>
</table>
## Specifications

<table>
<thead>
<tr>
<th></th>
<th>Galvo mode</th>
<th>Piezo mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lateral feature size</td>
<td>≤ 200 nm</td>
<td>≤ 200 nm</td>
</tr>
<tr>
<td>Vertical feature size</td>
<td>≤ 1500 nm</td>
<td>≤ 1000 nm</td>
</tr>
<tr>
<td>Writing speed</td>
<td>Typ. 10 mm/s</td>
<td>Typ. 100 µm/s</td>
</tr>
<tr>
<td>Range</td>
<td>Ø 200 µm</td>
<td>300x300x300 µm³</td>
</tr>
<tr>
<td>Accessible writing area</td>
<td>100x100 mm²</td>
<td>100x100 mm²</td>
</tr>
</tbody>
</table>
Fabrication procedure

(I) Objective

- Cover glass
- Monomer
- fs laser beam

(II) Monomer

- fs laser beam
- Polymer

(III) Developer

- 3D polymeric structure

(IV)
Feature size

- Resolution: ~ 100 nm
- Methods for making sub-resolution features
  - With additional radical quenchers
  - Using highly sensitive initiator
  - Repolymerization
  - Combined with stimulated emission depletion (STED)
Materials

- Compositions
  - Photoinitiators
  - Monomer
  - ...

- Requirements
  - Transparent in the visible and near infrared regions
  - Fast curing speed so that only the resin in the focal point is polymerized
  - Resisting to the solvent used in the later washout process
  - Suitable mechanical property and thermal stability to main the shape
Material capability: polymer

- Multiphoton induced polymerisation
- Multiphoton induced photoreduction of metal ions
- Common metals: Ag and Au

\[
\text{HAuCl}_4 \cdot \text{H}_2\text{O} \rightarrow \text{Au nanoparticles}
\]

1\textsuperscript{st} stage: Nucleation
2\textsuperscript{nd} stage: Growth
3\textsuperscript{rd} stage: Aggregation
Material capability: hybrid

Polymer resin

Metallic salts/acids
  e.g. H\textsubscript{AuCl\textsubscript{4}}

Polymerization
  Two-photon simultaneously induced
  Metal reduction

\[ \text{SU8 + Au} \]

\[ \text{IP-L + Au} \]

EDX mapping: Au
Material capability: nanomaterials

- Small amount of nanomaterials mixed with polymer resin to increase the functionality
- Format: nanoparticles, quantum dots, carbon nanotube…

Patterns with (c) CdSe and (d) CdSe/ZnS QDs for colour display devices

Magnetic turbine with Fe$_3$O$_4$ NPs

## Table 1. Materials used for two-photon cross-linking and two-photon polymerization.

<table>
<thead>
<tr>
<th>Type</th>
<th>Hydrogel</th>
<th>Polymer</th>
<th>Photoinitiator</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nondegradable</td>
<td>No</td>
<td>ORMOCER®/Ormocomp®</td>
<td>Irgacure® 369</td>
<td>[36, 87, 102]</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>SR368+SR499</td>
<td>Lucin® TPO-L</td>
<td>[103, 104]</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>PEGda</td>
<td>Irgacure® 369</td>
<td>[97, 105, 111, 132]</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>PEGda</td>
<td>WSPl⁺</td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>Accura® SI10</td>
<td>Not reported</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>Ti- and Zr-based sol-gels</td>
<td>Irgacure® 369</td>
<td>[113, 133]</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>Chitosan-doped</td>
<td>Lucin® TPO-L</td>
<td>[134]</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>UDMA</td>
<td>Irgacure® 369</td>
<td>[90]</td>
</tr>
<tr>
<td>Biodegradable</td>
<td>No</td>
<td>PCL based</td>
<td>Michlers ketone</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>gelMOD</td>
<td>Irgacure® 2959⁺</td>
<td>[92, 95]</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>OLMA</td>
<td>Irgacure® 369</td>
<td>[90]</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>PLA based</td>
<td>Michlers ketone</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>BSA and fibrinogen</td>
<td>RoseBengal⁺</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>Biotinylated BSA</td>
<td>Flavin mononucleotide⁺</td>
<td>[135]</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>Collagen</td>
<td>Benzophenone dimer⁺</td>
<td>[136]</td>
</tr>
</tbody>
</table>

*Water-soluble and biocompatible photoinitiators.

BSA: Bovine serum albumin; gelMOD: Methacrylated gelatine; OLMA: Methacrylated oligolactones; PEGda: Poly(ethylene glycol) diacrylate; PLA: Poly(lactic acid); SR368: Tris (2-hydroxyethyl) isocyanurate triacrylate; SR499: Ethoxylated (6) trimethylpropane triacrylate; UDMA: Urethandimethacrylate; WSPl: 1,4-bis[4’-(N,N-bis[6[bis[trimethylammoniumiodide-6-hexyl]-amino]hexyl]amino)styryl]-2,5-dimethoxybenzene.
Material capability: Casting from polymer

Positive photoresist → 3D fabricate by multiphoton lithography → Deposit Au

Remove polymer mould by plasma etching
Applications:

Scaffolds for cell biology

Applications:

Micro-needles for drug delivery

Int J App Cera Tech 4 (2007) 22; Laser Zenturm Hannover
Applications:

Functional micro-channels

Fabricate cell-sized 3D structures in the centre channel (*black dashed lines*)

Applications:

Magnetic micro-actuator

Applications:

Optical-driven micro-rotor

Optical trapping and rotation

Optical-driven micropump action in a microfluidic channel

Applications:

Chemical-driven micro-actuator

Gecko-mimicking surface for adhesive
Combined with jetting

- PEGDA film (~20 µm thick): jetting + UV curing
- IP-L micro structure on top of PEGDA thin film: two-photon polymerisation
Applications:

Connection & bonding

Applications:

Micro-optics

Microlens arrays & their arrays of miniaturized “F” images

Fresnel zone plate

Fabricate on the tip of an optical fibre

Axicon lens

**Applications:**

**Waveguides**

**Multimode waveguide on PCB**
Data transfer rate: 7 Gbit/s

**Plasmonic waveguide**

A waveguide is placed around a bubble (~ 80 µm)

Applications:
Photonic crystals

**Applications:**

Optical metamaterials

**Manufacturing routes:**

- Two-photon polymerization + metal coating
- Photopolymerization & photoreduction simultaneously

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Perfect absorber

*References*

- Phy Rev B 88 (2013) 115105
- Adv Mater 25 (2013) 3994
- IEICE Electronics Express 9 (2012) 34
- Opt Mater Exp 1 (2011) 1548
- Acs Nano 5 (2011) 1947
Applications:

Mechanical metamaterials

- Artificial structures with mechanical properties defined by structures rather than their composition
- Nanolattice: strong & lightweight

Strength up to 280 MPa!

$L = 5 \mu m; a = 650 \text{ nm}; t = 10 \text{ nm}$

Science 345 (2014) 1322; PNAS 111 (2014) 2453
Applications:
For fun...

Nanoscribe, Karlsruhe Institute of Technology, Vienna Institute of Technology, Jonty Hurwitz
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