Multiphoton lithography based 3D micro/nano printing

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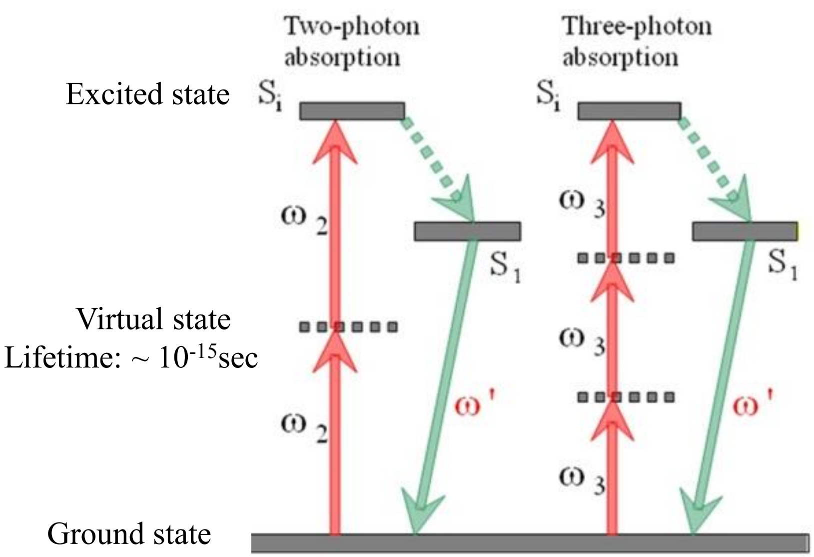
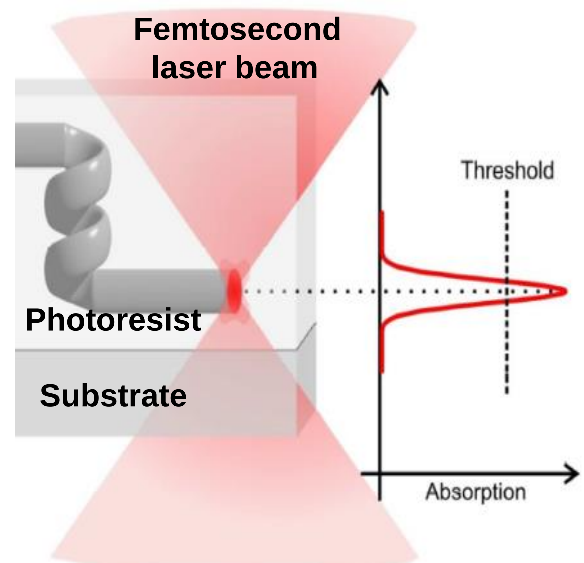
Multiphoton lithography

- 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

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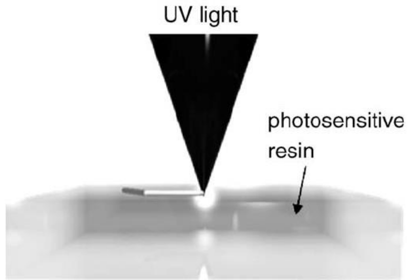
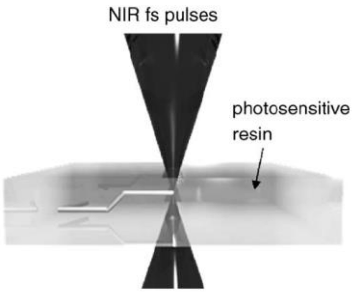
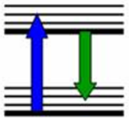
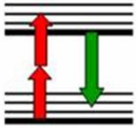
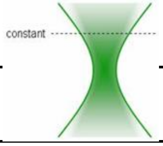
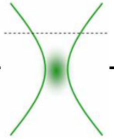
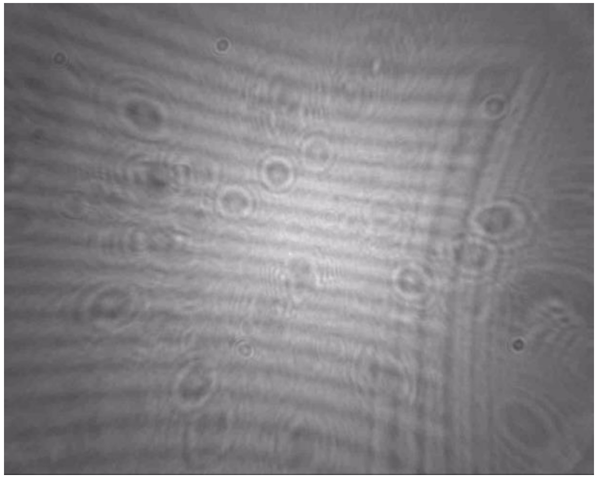
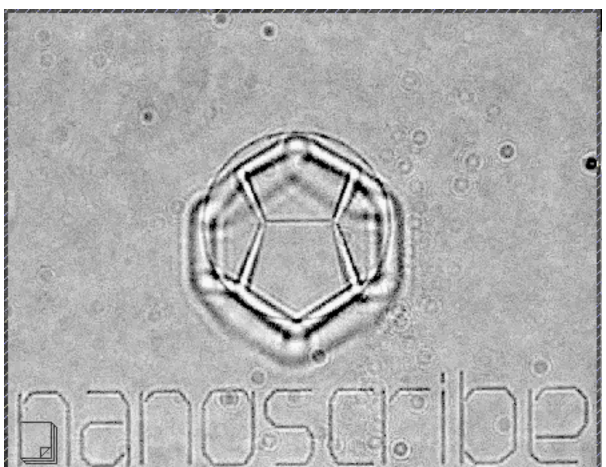
	Micro stereolithography	Multiphoton lithography
		
Essential elements	**CAD design, 2D layer preparation function, laser scanning & controlling system with monitoring devices**	
Mechanism for polymerisation	**One-photon absorption** (Linear absorption) 	**Multi-photon absorption** (Non-linear absorption) 
Laser type	**UV laser** 	**NIR femtosecond laser** 
Resolution	**~ 1 μm**	**~ 100 nm**
Strategy for 3D fabrication	**Polymerisation at the surface → layer-by-layer approach**	**Polymerisation at any desired location → Built 3D structure 'recording' the beam path**

Systems



Nanoscribe



Specifications	Galvo mode	Piezo mode
Lateral feature size	≤ 200 nm	≤ 200 nm
Vertical feature size	≤ 1500 nm	≤ 1000 nm
Writing speed	Typ. 10 mm/s	Typ. 100 µm/s
Range	Ø 200 µm	300x300x300 µm^3
Accessible writing area	100x100 mm^2	100x100 mm^2

Fabrication procedure

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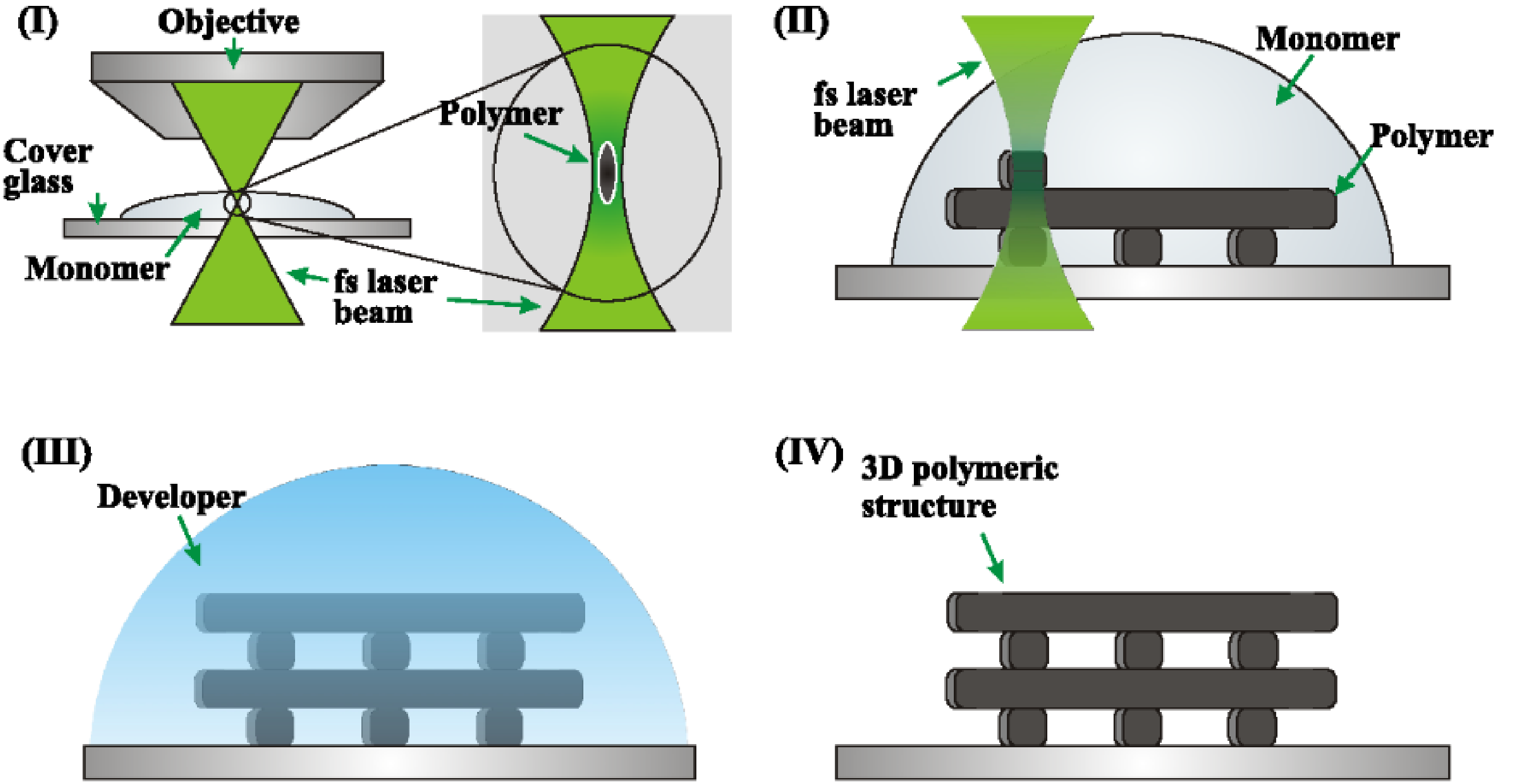

J Biomed Optics 17 (2012) 081405

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Feature size

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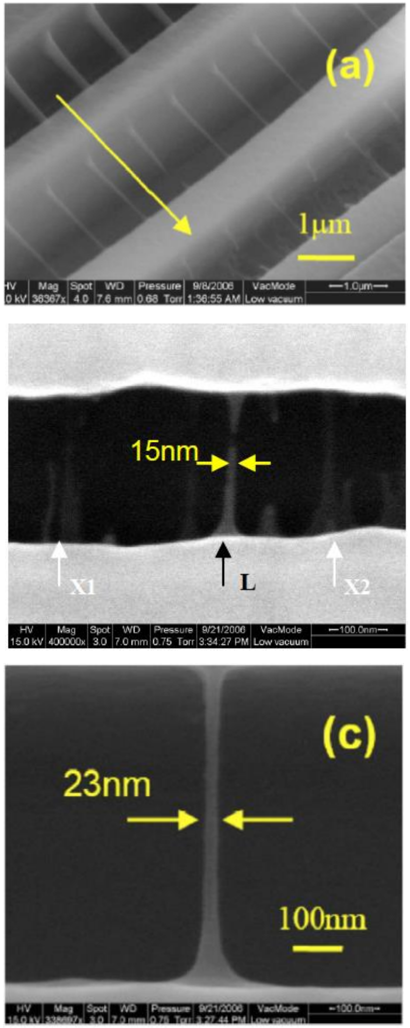
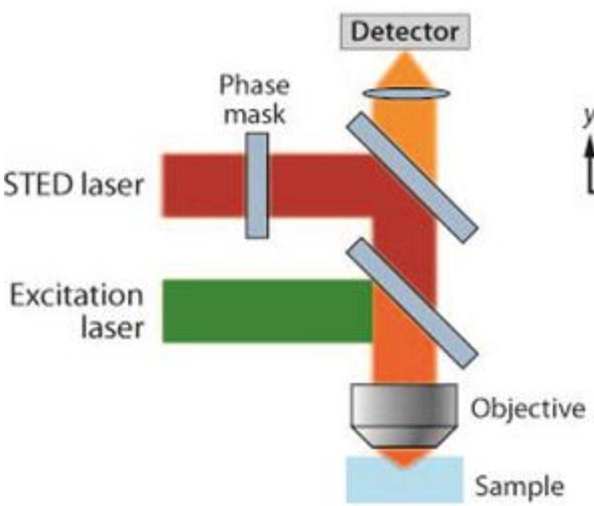
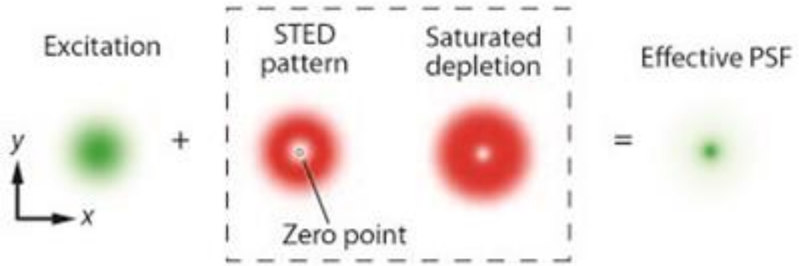
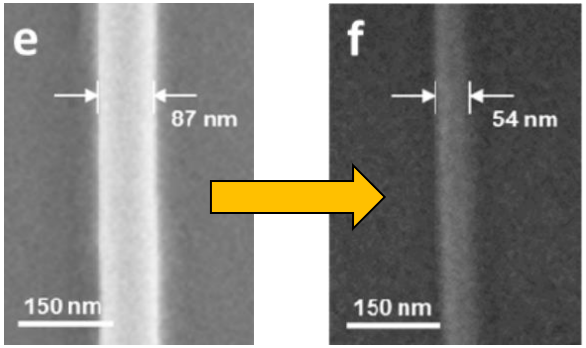
- Resolution: ~ 100 nm
- Methods for making sub-resolution features
  - With additional radical quenchers
  - Using highly sensitive initiator
  - Repolymerization
  - Combined with stimulated emission depletion (STED)









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Nanotechnology 16 (2005) 846; Appl Phys Lett 89 (2006) 173133; 90 (2007) 071106; Annu Rev of Biochem 78 (2009) 993; Optics Express 21 (2013) 10831; Nano Letters 13 (2013) 5672

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

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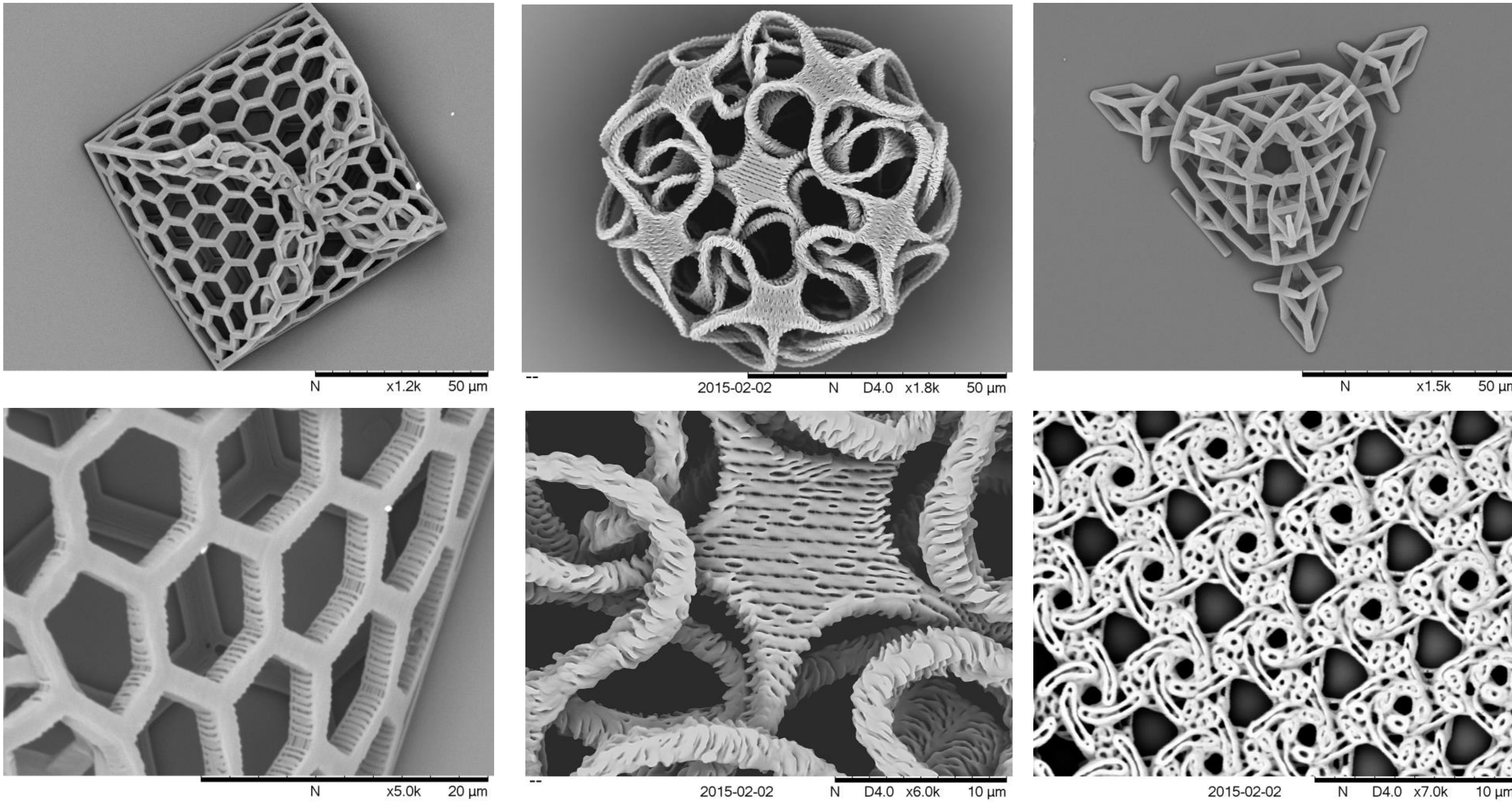
- Multiphoton induced polymerisation



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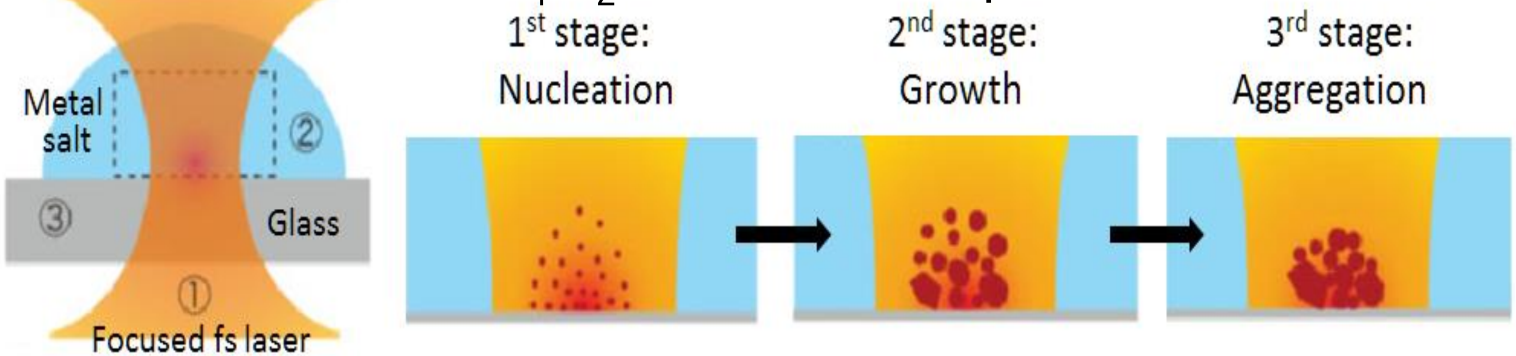
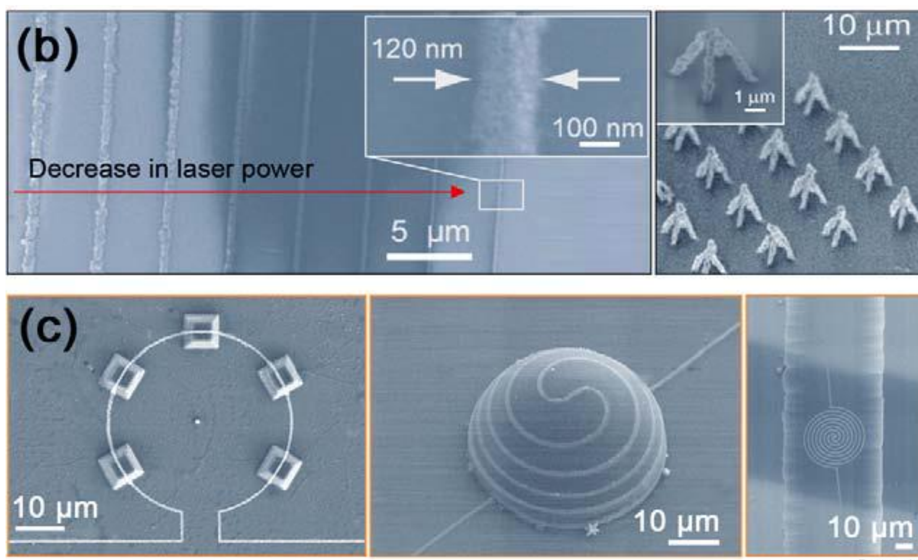
Material capability: metal

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

$HAuCl_4.H_2O \rightarrow$ Au nanoparticles





Nano Today 5 (2010) 435

Material capability: hybrid

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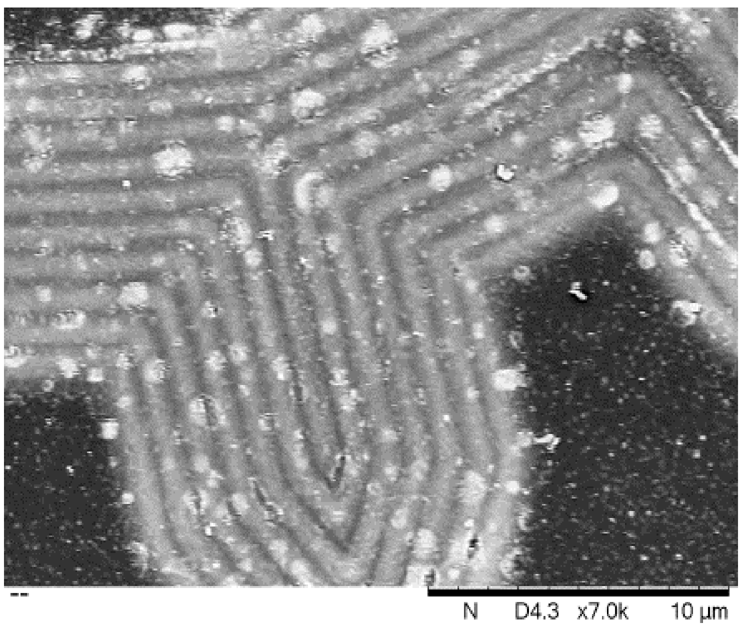
Polymer resin
+
Metallic salts/acids
e.g. $HAuCl_4$

Polymerization

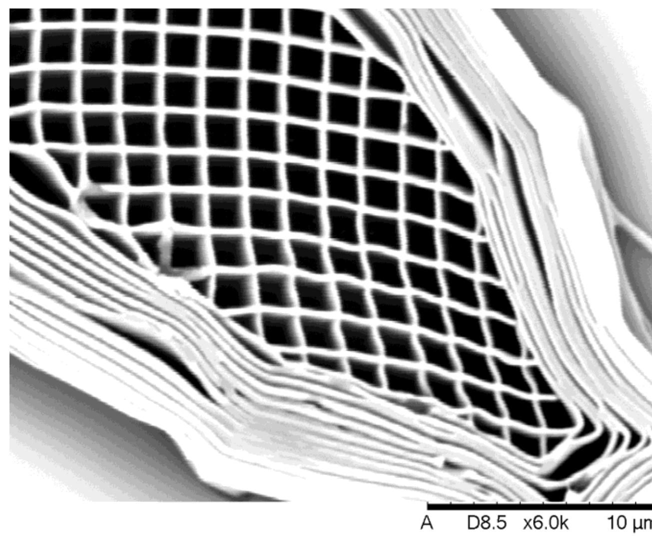
Two-photon simultaneously induced

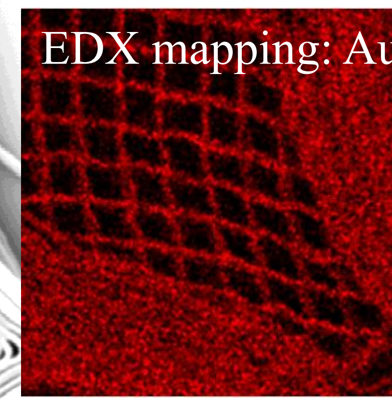
Metal reduction

Polymer
Metal



SU8 + Au





IP-L + Au

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Material capability: nanomaterials

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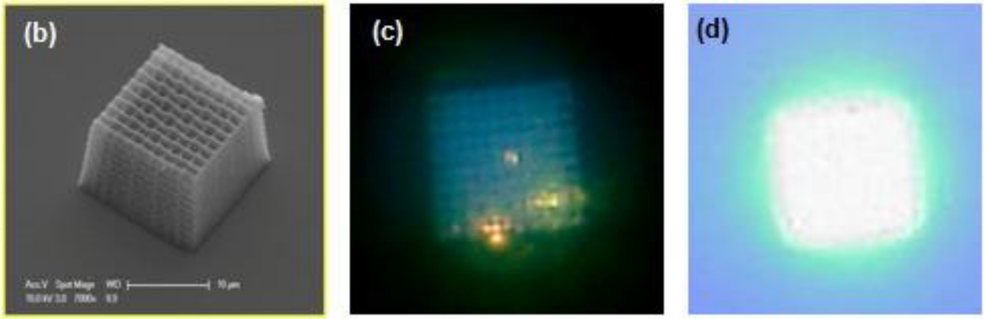
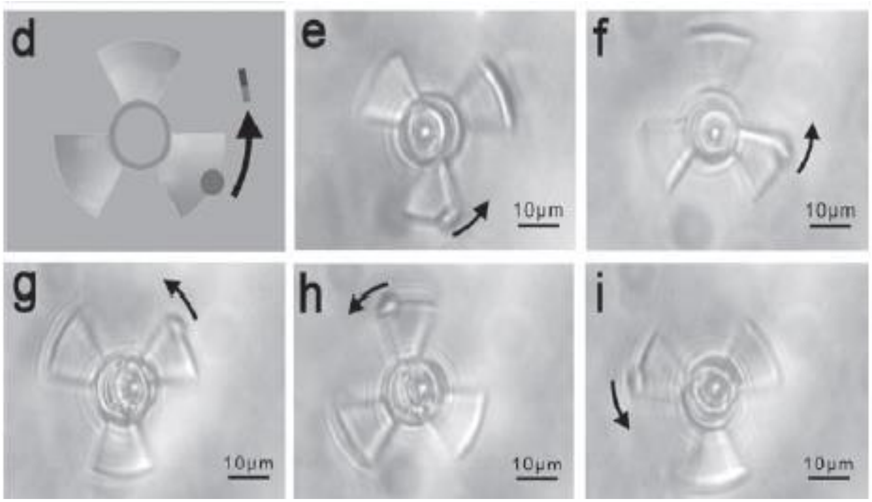
- Small amount of nanomaterials mixed with polymer resin to increase the functionality
- Format: nanoparticles, quantum dots, carbon nanotube…



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



Magnetic turbine with Fe_3O_4 NPs

Optical Materials Express 2(2012) 519; Adv Materials 22 (2010) 3204;

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Material capability: biomaterials

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

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

†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) trimethylolpropane triacrylate; UDMA: Urethandimethacrylate; WSPI: 1,4-bis[4′-(*N,N*-bis[6′[bis[trimethylammoniumiodide-6-hexyl]-aminohexyl]amino)styryl]-2,5-dimethoxybenzene.

Expert Rev Med Devices 9 (2012) 613

Material capability:

Casting from polymer

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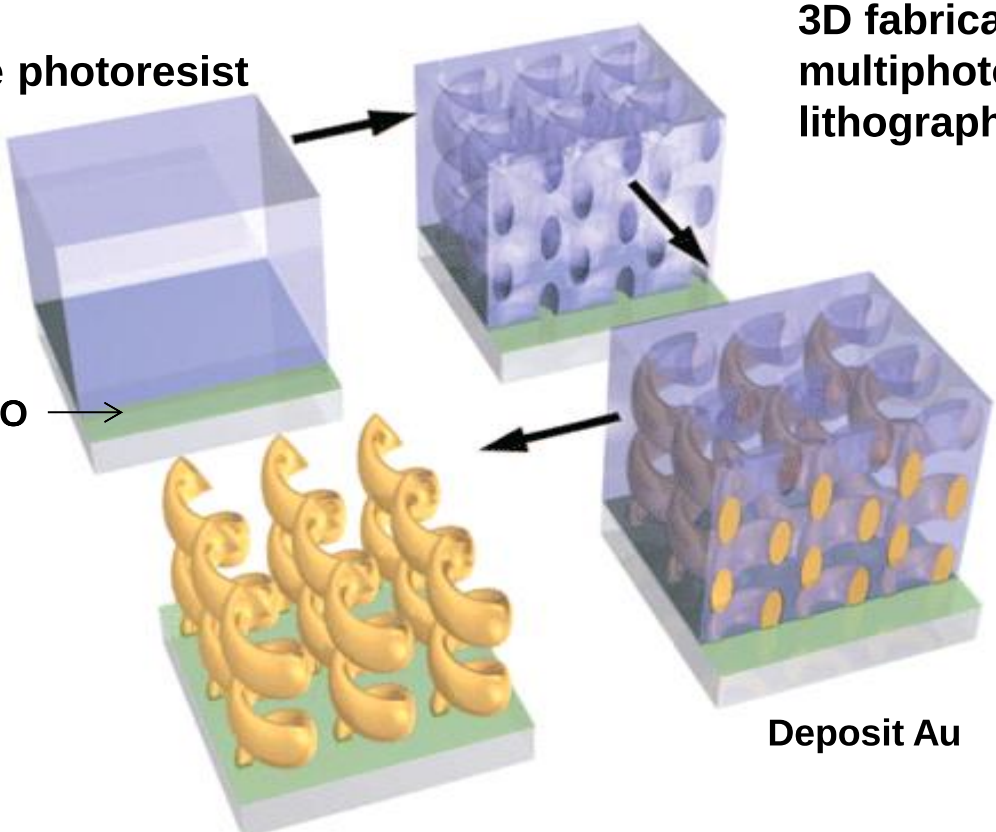
Positive photoresist

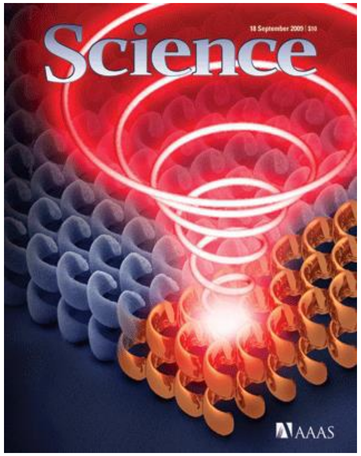
3D fabricate by multiphoton lithography

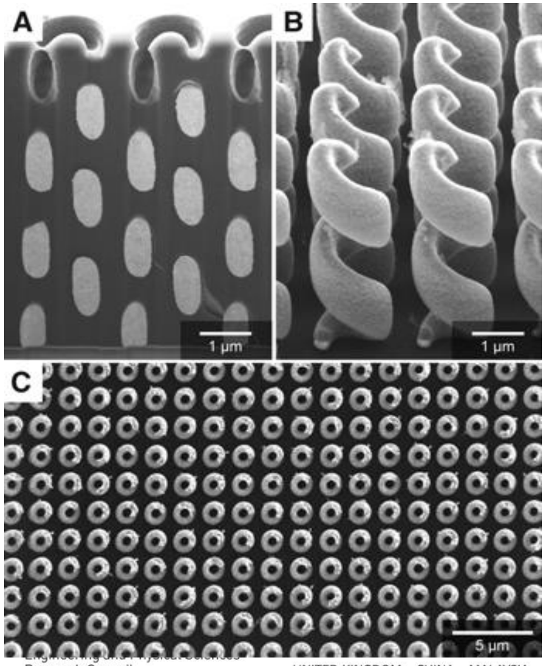
ITO



Deposit Au

Remove polymer mould by plasma etching





Science 325 (2009) 1513

Applications

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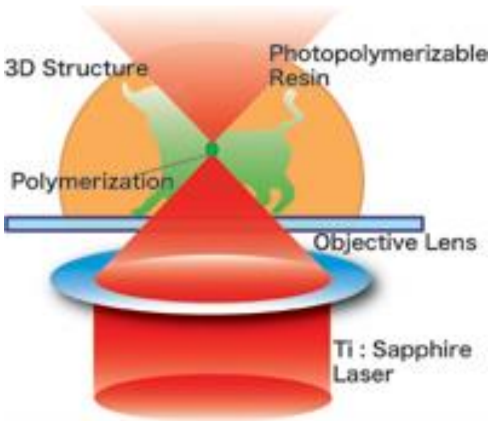
Photonics

Cell biology

Biomimetics

Microfluidics

Micro-mechanics



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Applications:

Scaffolds for cell biology

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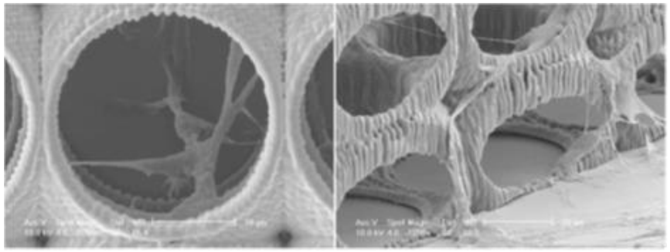

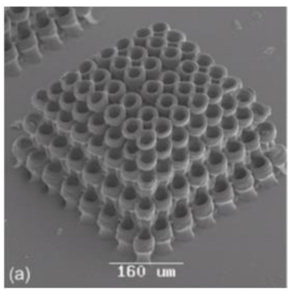

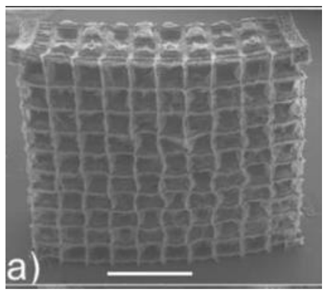

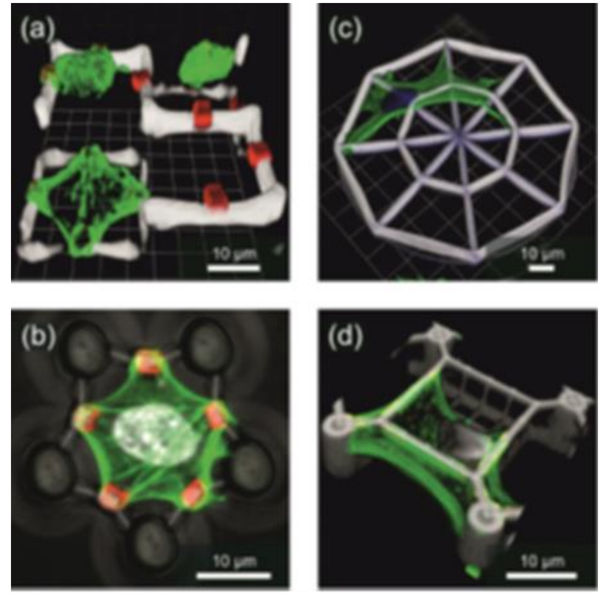

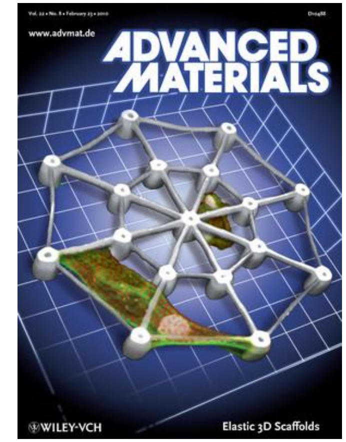

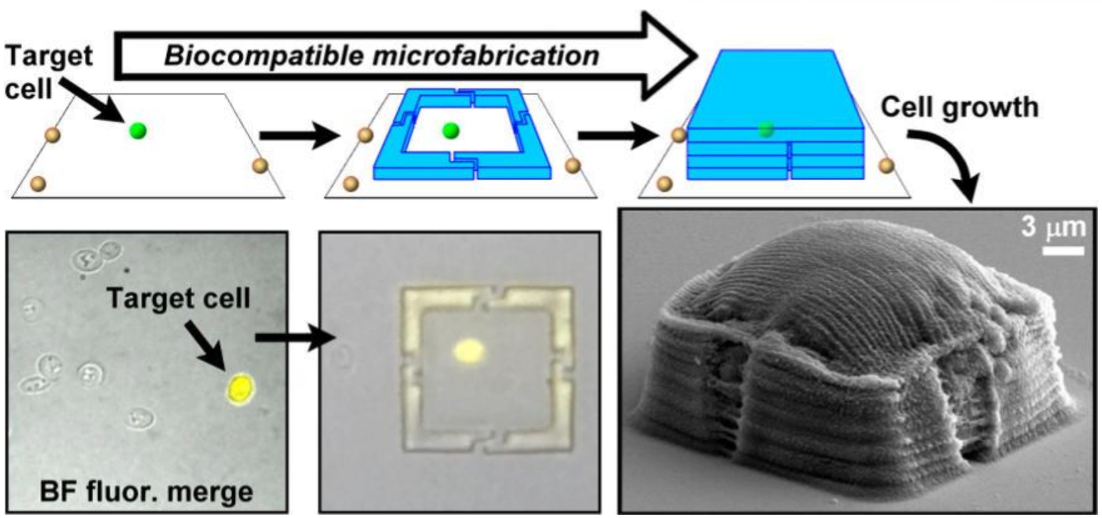

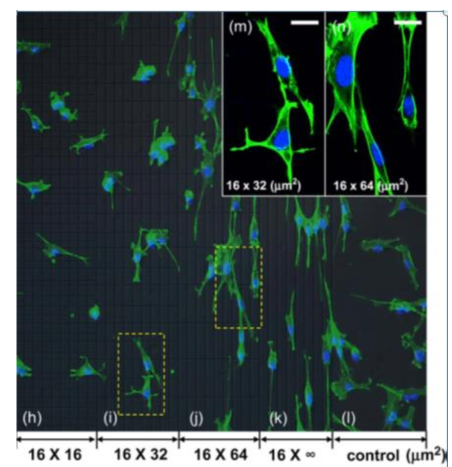

J Micromech Microeng 22 (2012) 115016; Macromol Biosci 12 (2012) 1301; Anal Chem 84 (2012) 8985;
Acta Biomaterialia 7 (2011) 967; Biomacromolecules 12 (2011) 851; Biomaterials 31 (2010) 4286; Adv Mater 22 (2010) 868

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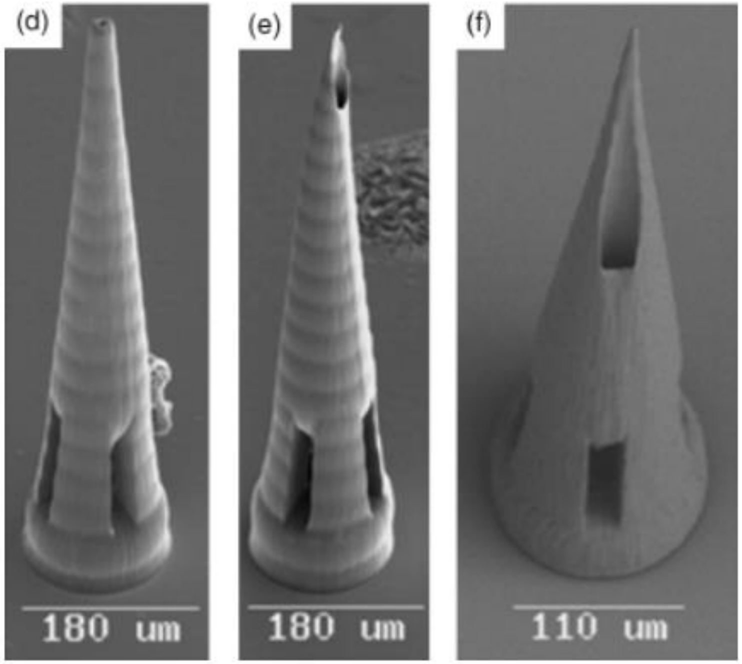
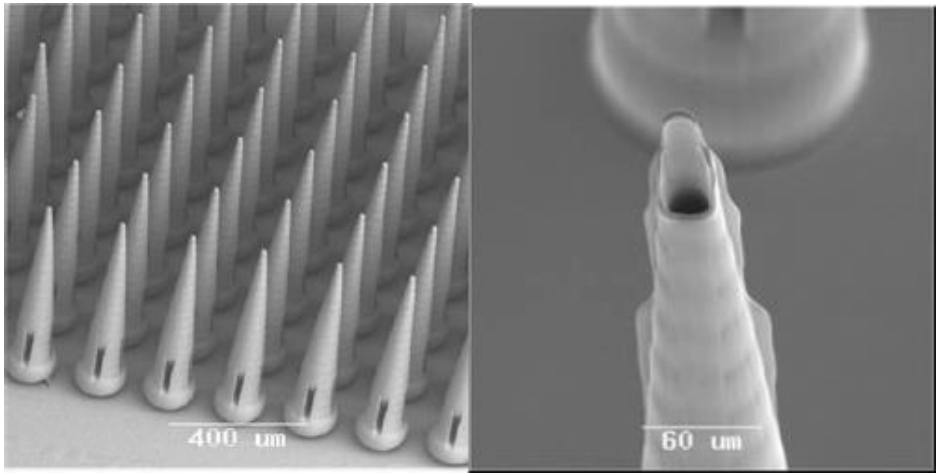
Applications:

Micro-needles for drug delivery





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

Applications:

Functional micro-channels

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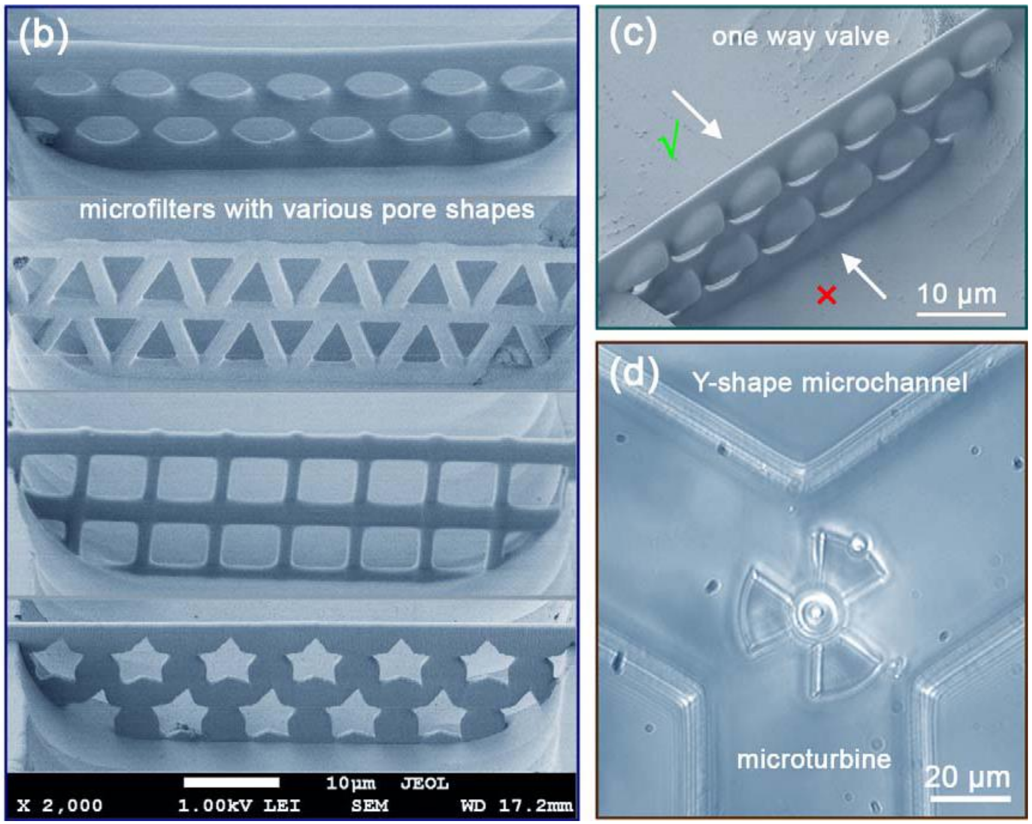
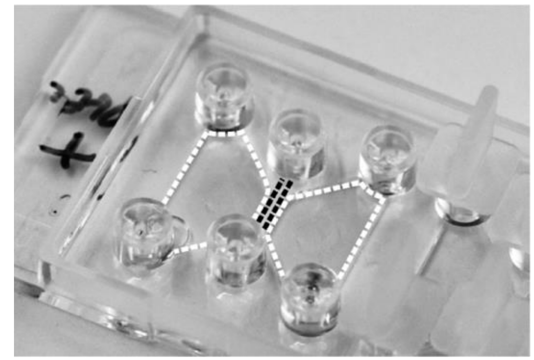
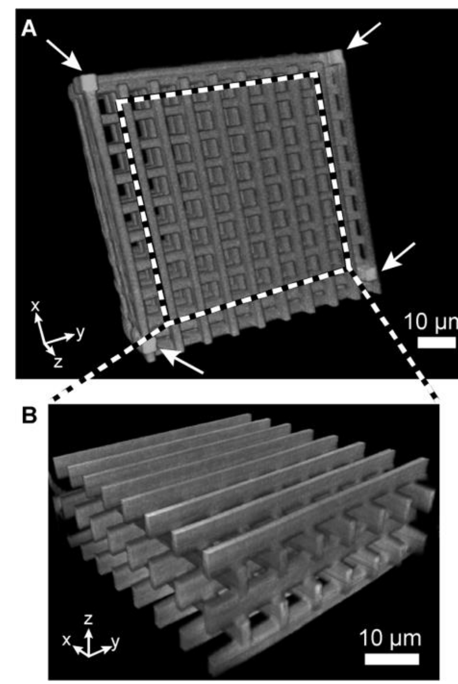
Fabricate cell-sized 3D structures
in the centre channel *(black dashed lines)*







Lab Chip 10 (2010) 1057; Lab Chip 10 (2010) 1993; Lab Chip 13 (2013) 4800

Applications:

Magnetic micro-actuator

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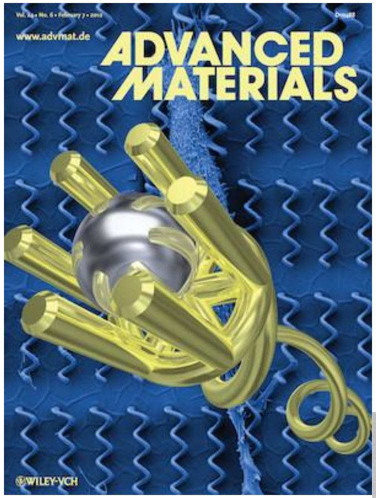

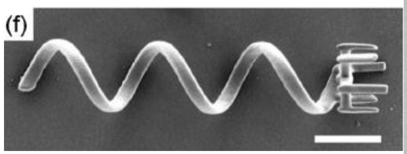

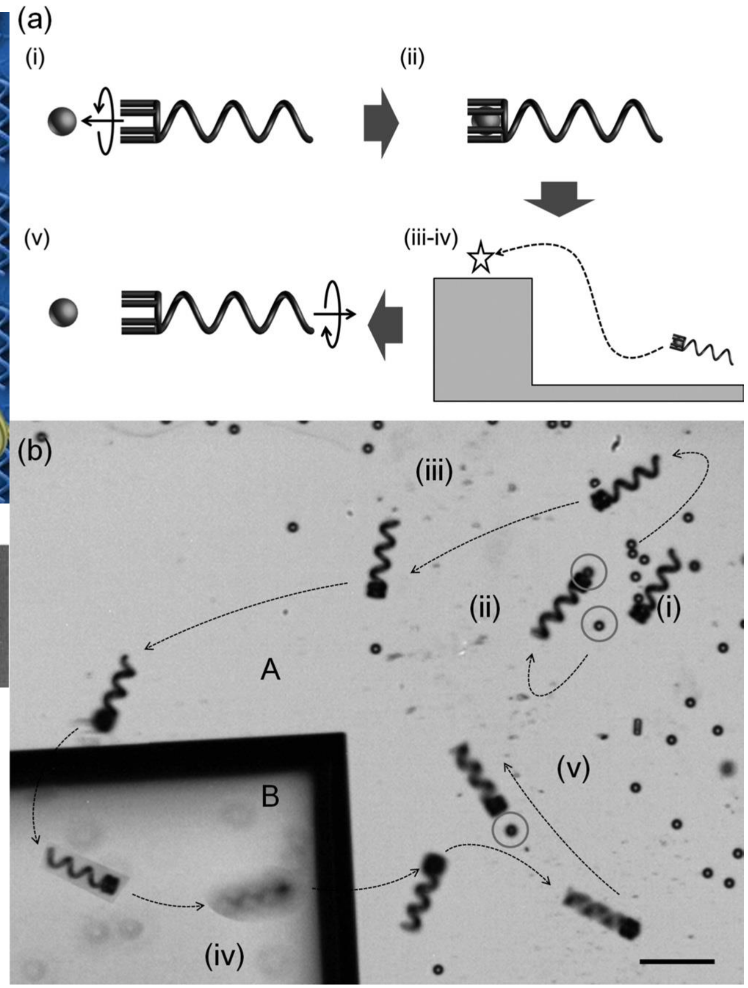

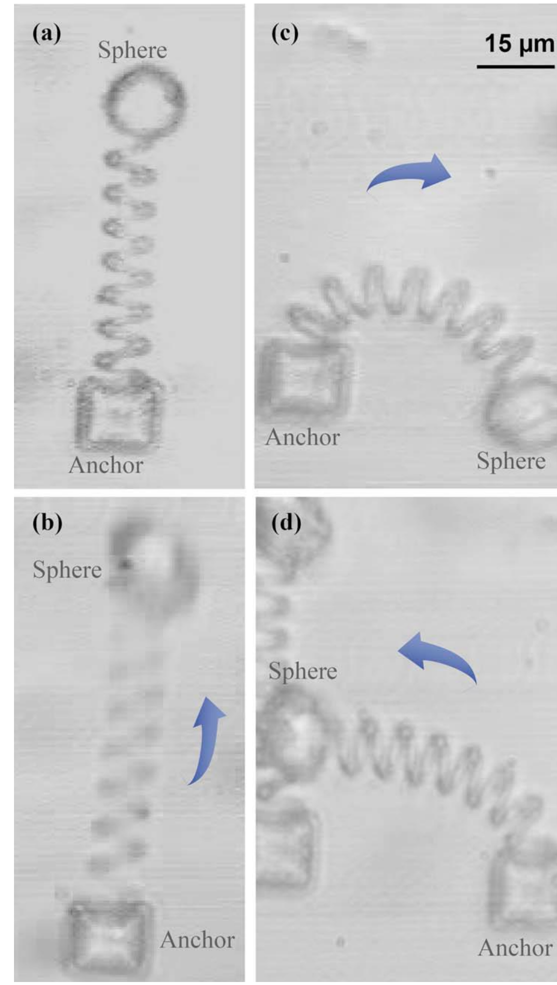

Adv Mater 24 (2012) 811; Opt Lett 34 (2009) 581

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Applications:

Optical-driven micro-rotor

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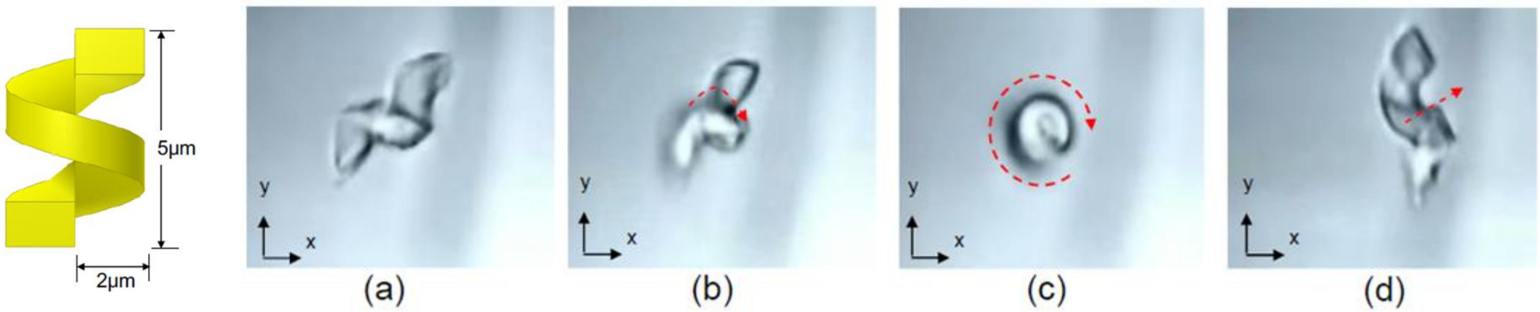
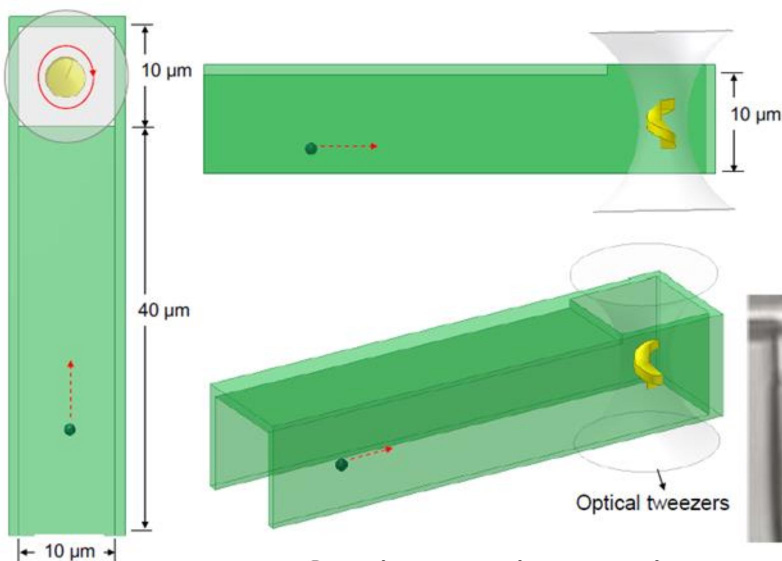
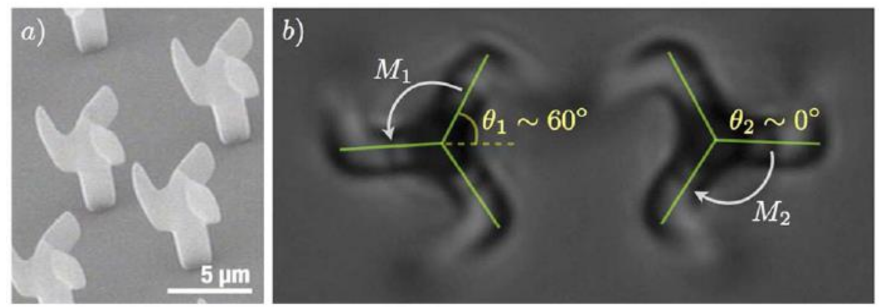
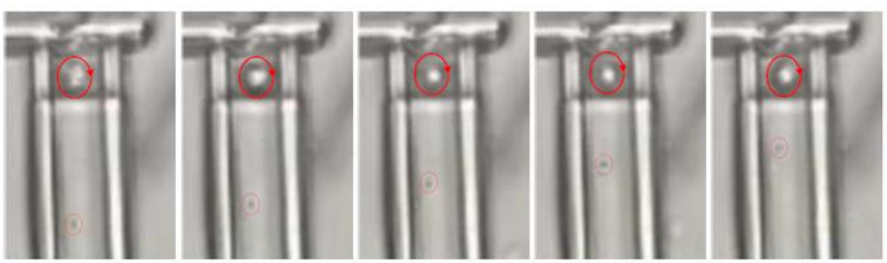
Optical trapping and rotation









Optical-driven micropump action in a microfluidic channel

Phys Rev Lett 109 (2012) 034104; Optical Express 19 (2011) 8267

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Applications:

Chemical-driven micro-actuator

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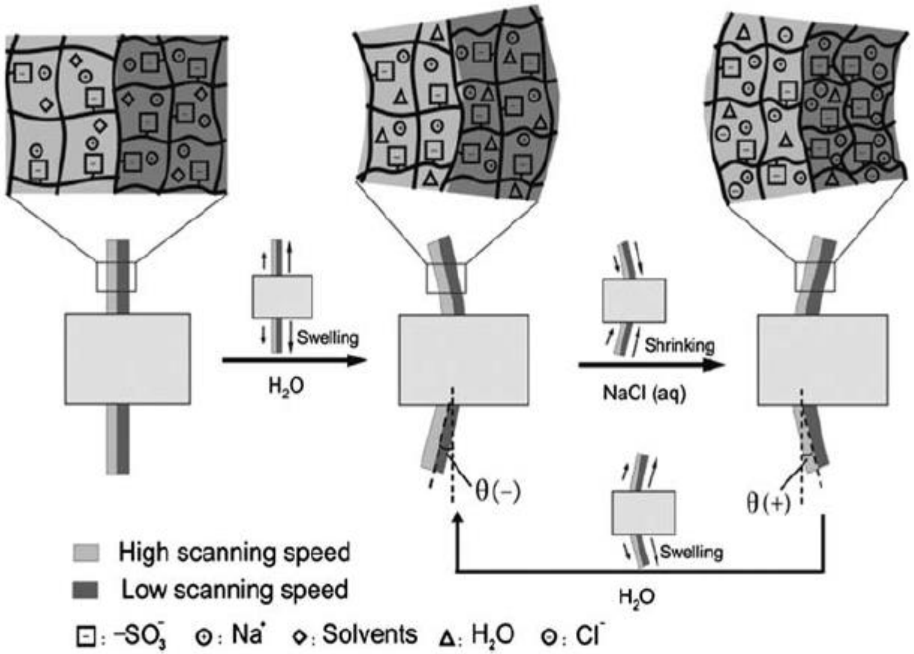

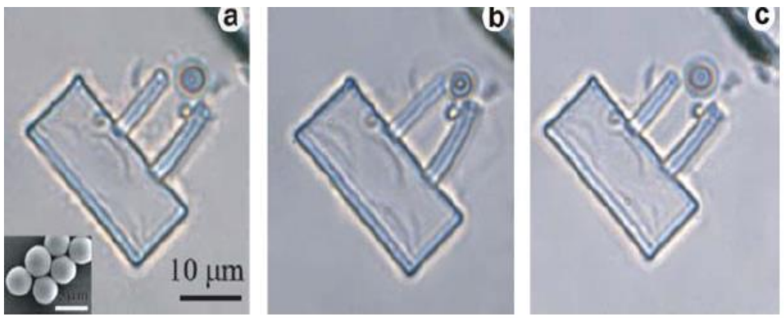

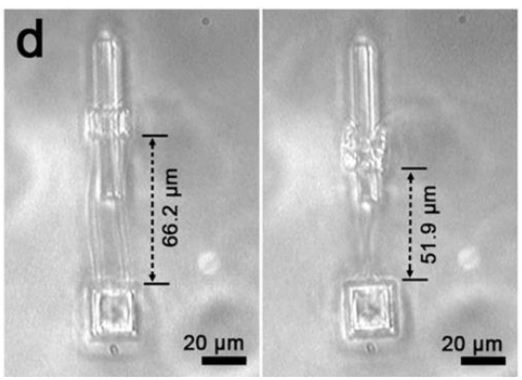

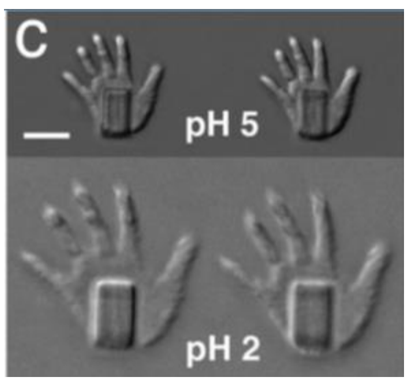

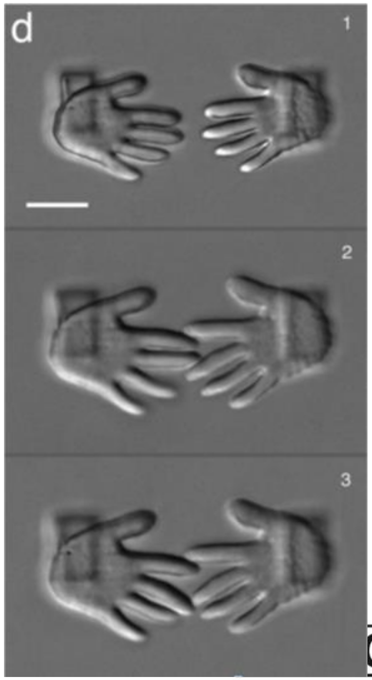

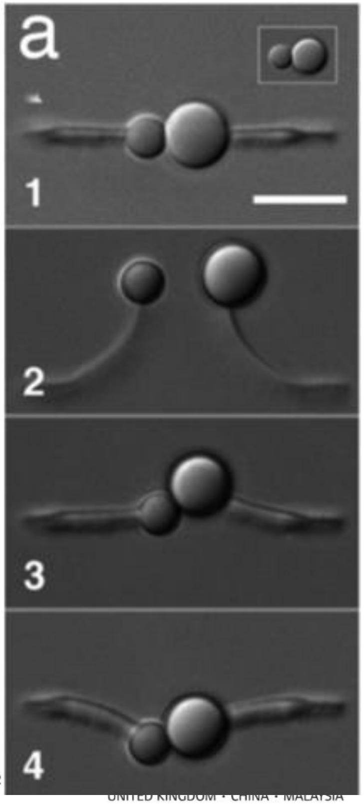

PNAS 105 (2008) 8850; Soft Matter 7 (2011) 10353; Phys Chem Chem Phys 13 (2011) 4835

Applications:

Biomimetics

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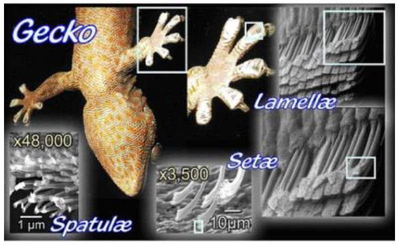
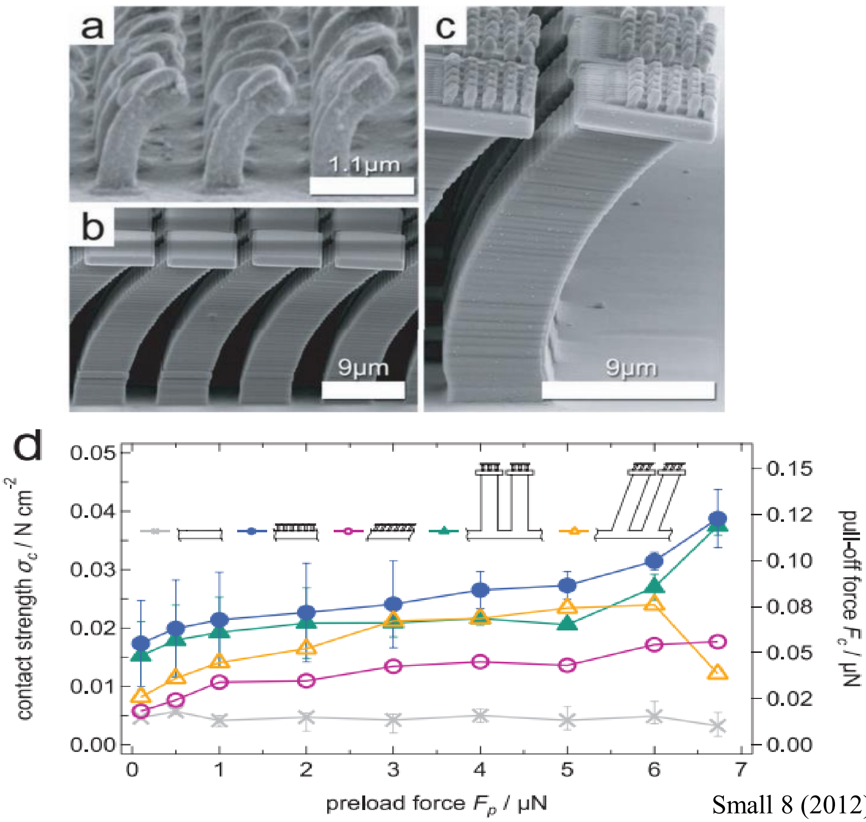
Gecko-mimicking surface for adhesive





Small 8 (2012) 3009

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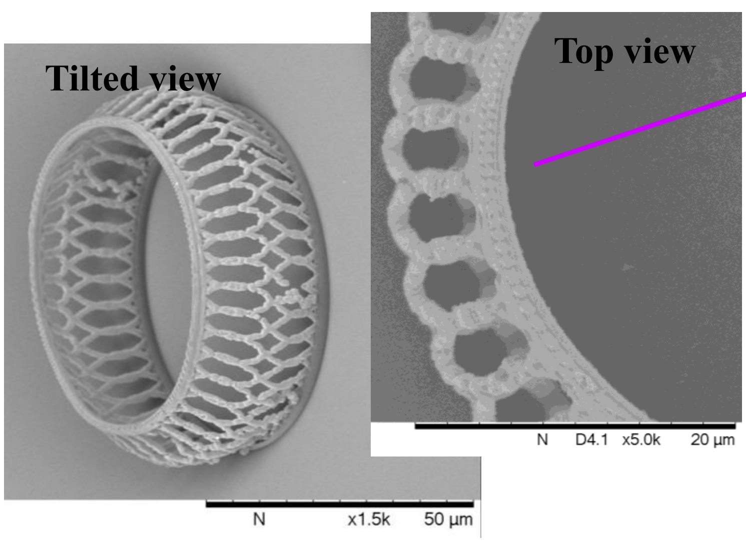
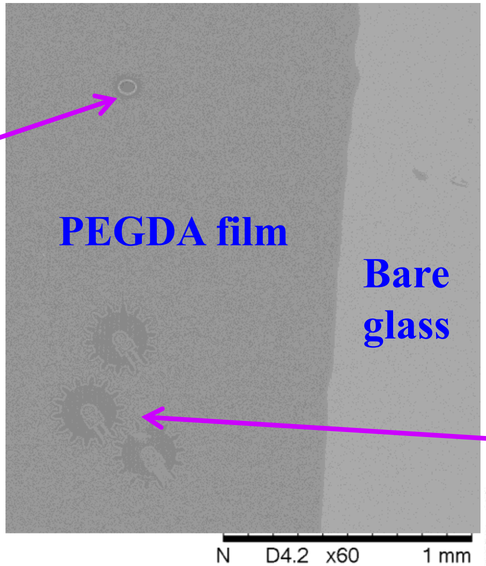
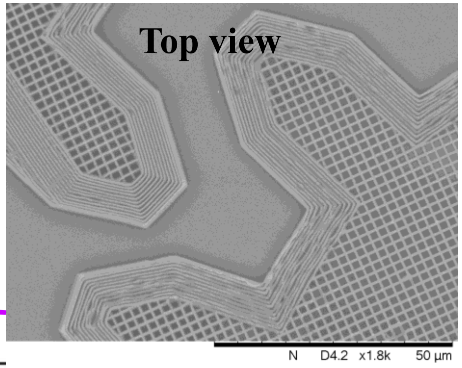
Combined with jetting

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







Applications:

Connection & bonding

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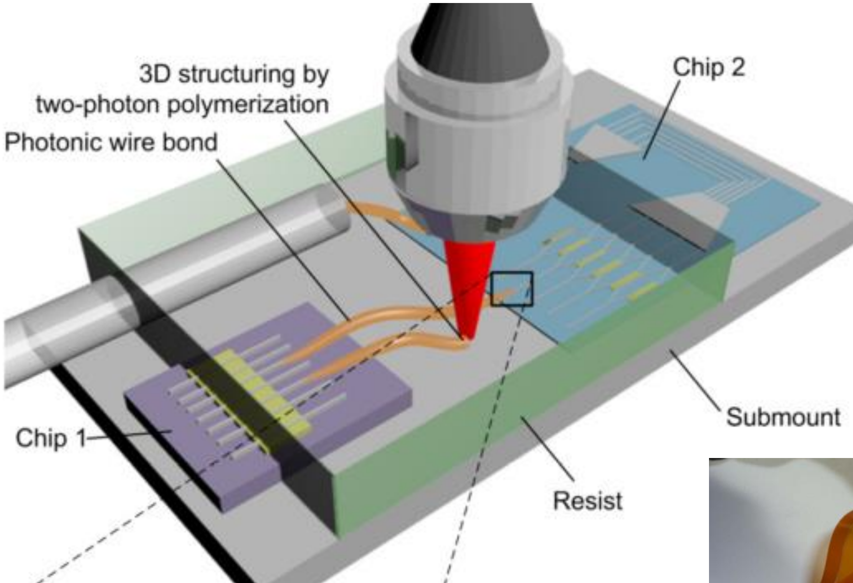

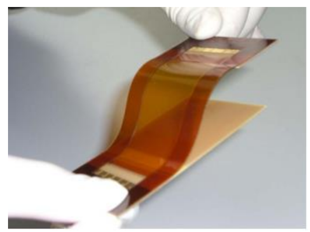

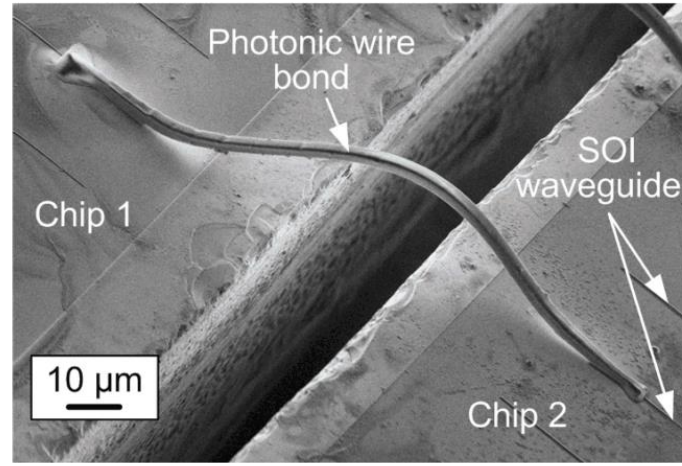

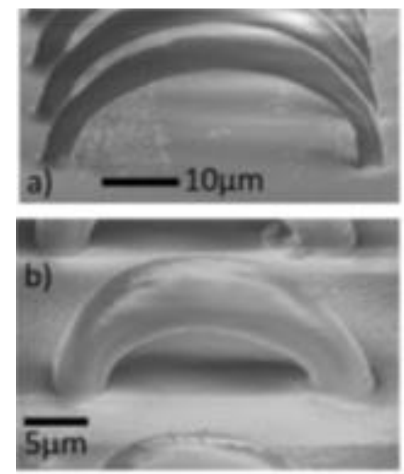

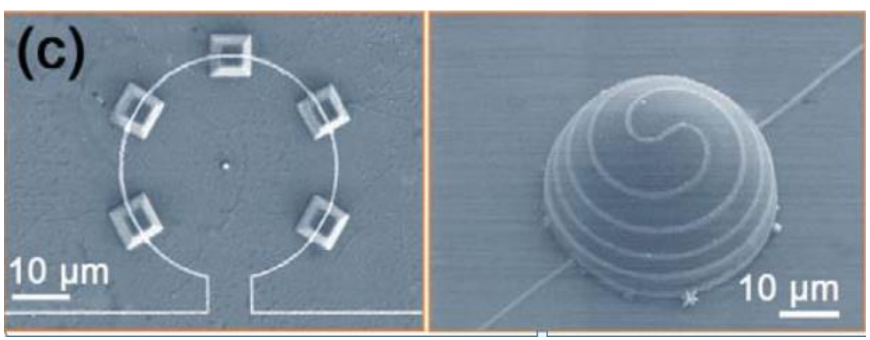

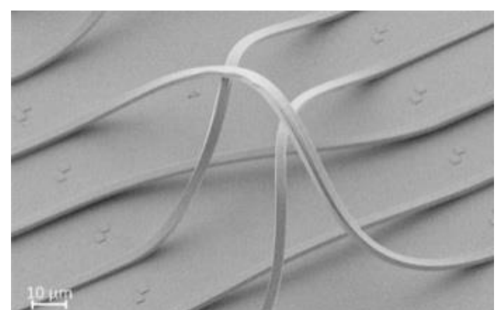

Appl Opt 52 (2013) 388; Opt Exp 20 (2012) 17667; Appl Phys Lett 100 (2012) 171102; Nano Today 5 (2010) 435

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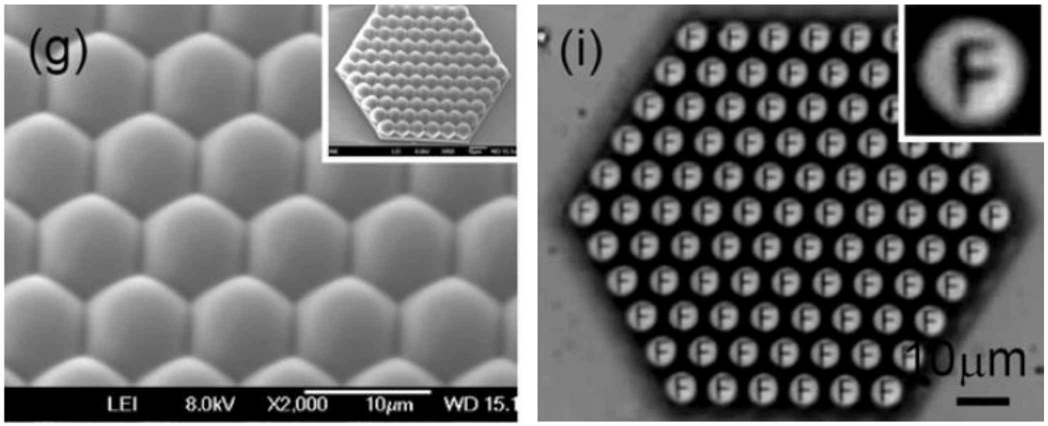
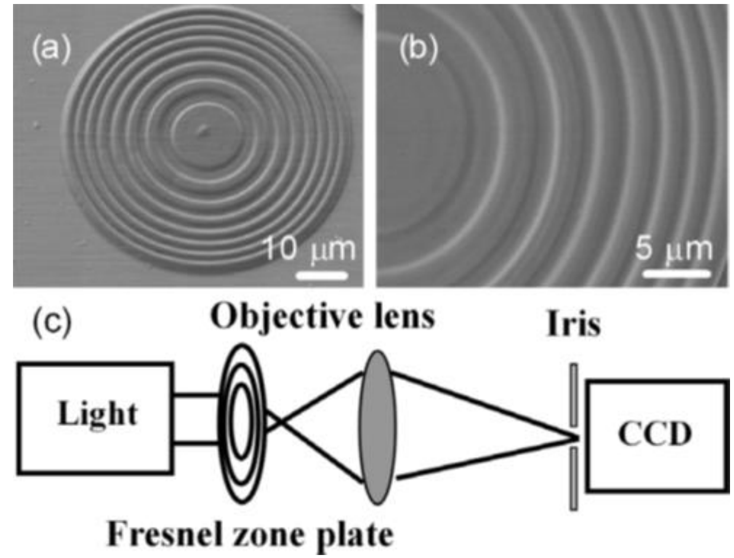
Applications:

Micro-optics

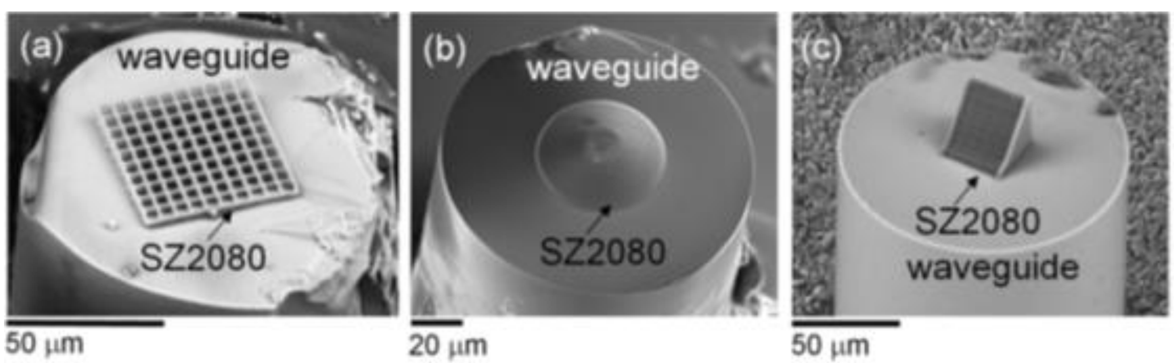
Microlens arrays & their arrays of miniaturized "F" images



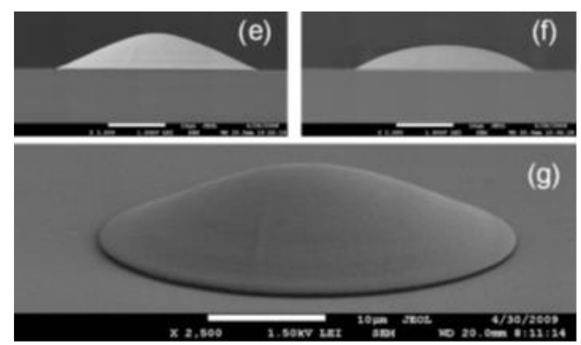
Fresnel zone plate



Fabricate on the tip of an optical fibre



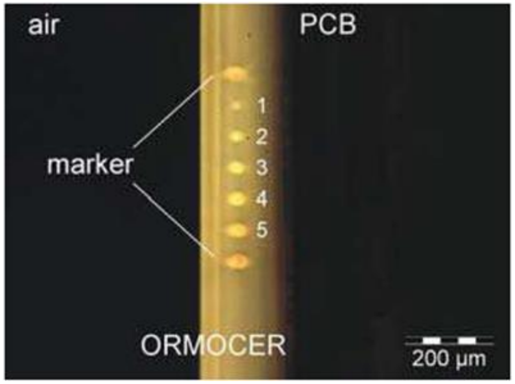
Axicon lens



Appl Phys Lett 97 (2010) 031109; J Opt 12 (2010) 035203; J Lightwave Tech 28 (2010) 1256 ; J Opt 12 (2010) 124010

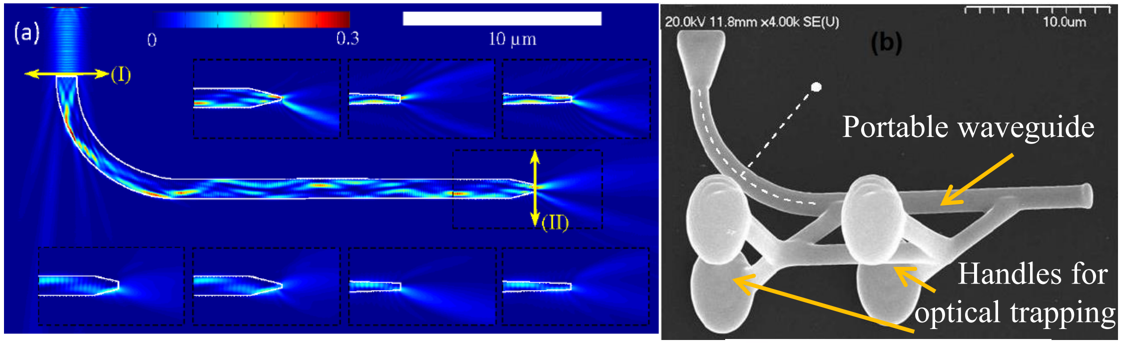
Applications:

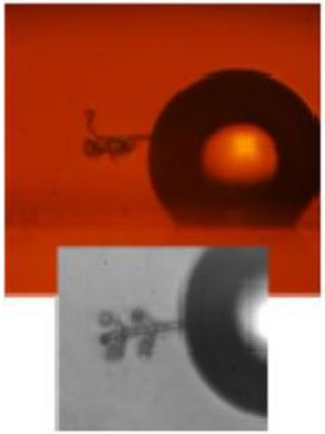
Waveguides



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

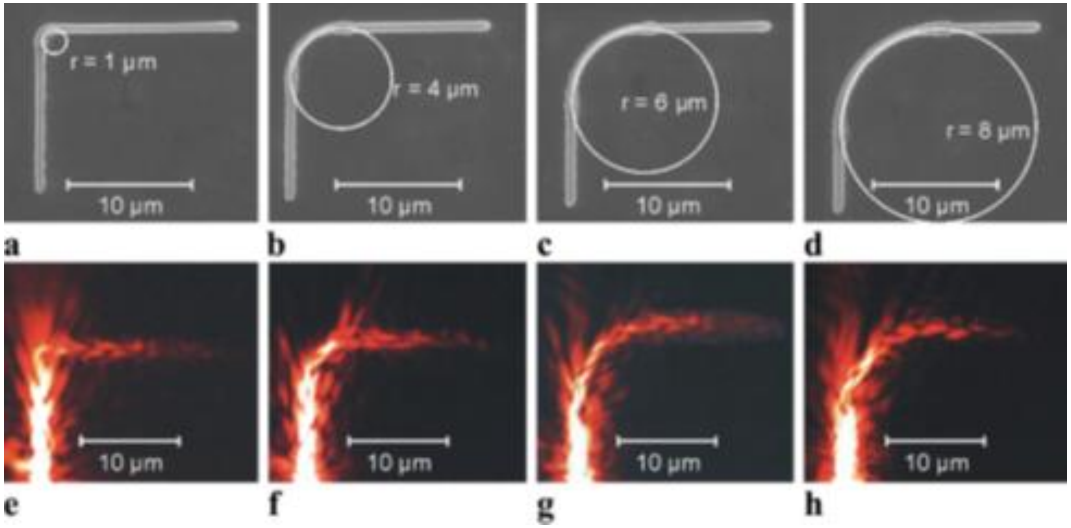
Portable waveguide





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

Plasmonic waveguide



Opt Expr 20 (2012) 2004; Appl Phys A 100 (2010) 347; Proceeding of SPIE (2008);

Applications:

Photonic crystals

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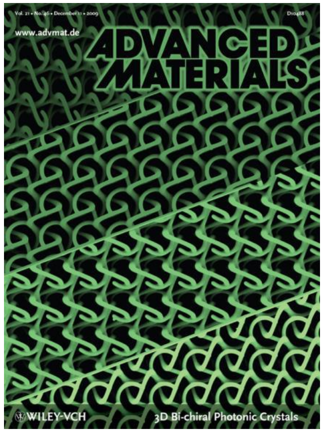

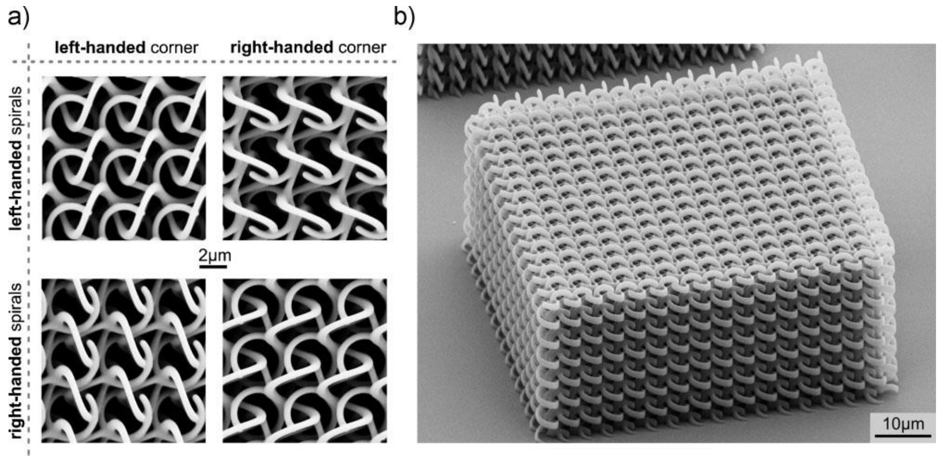

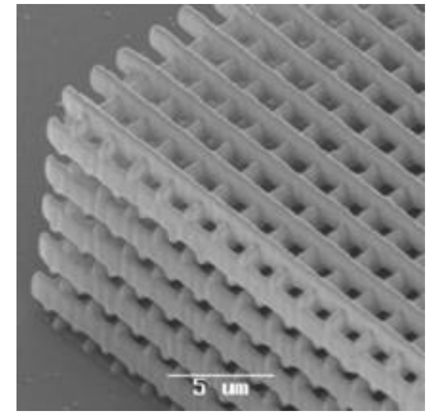

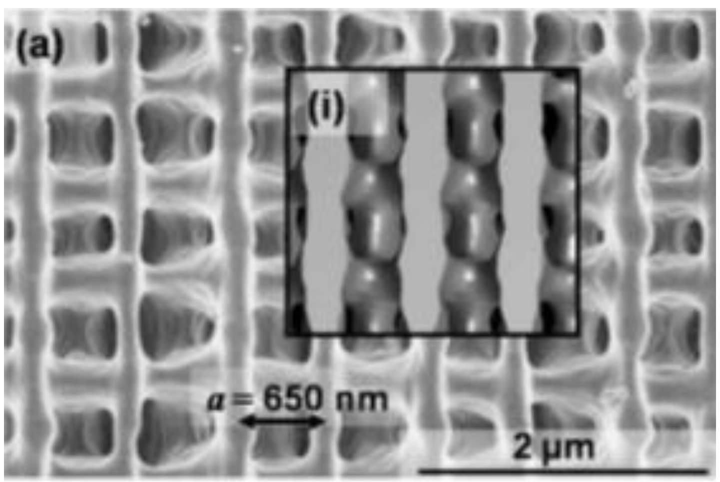

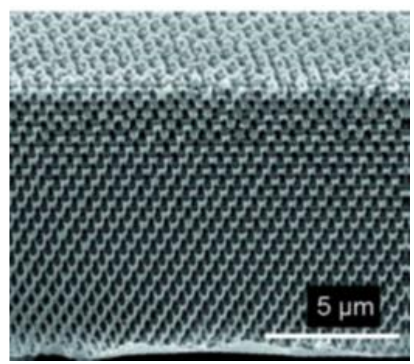

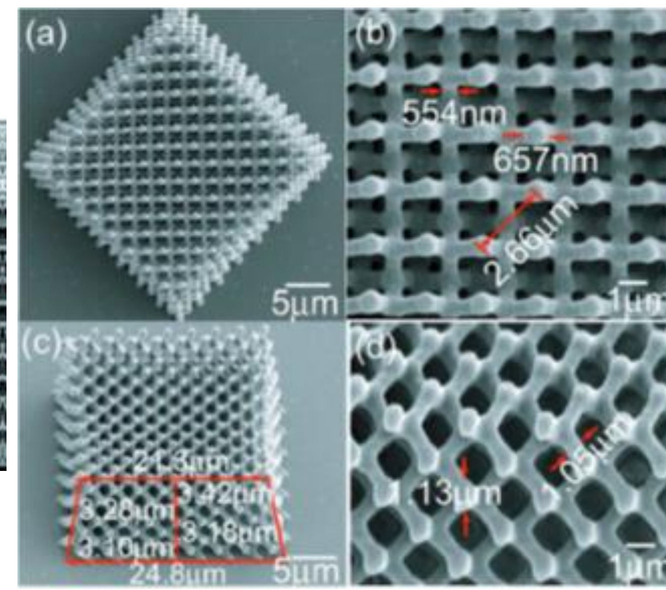

Adv Mater 21 (2009) 4680; Appl Phy Lett 94 (2009) 011101; Appl Phy A 93 (2008) 11; Optics Express 16 (2008) 15402; Optics Express 16 (2008) 20073;

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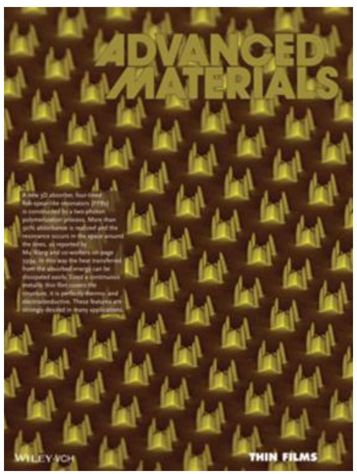
Applications:

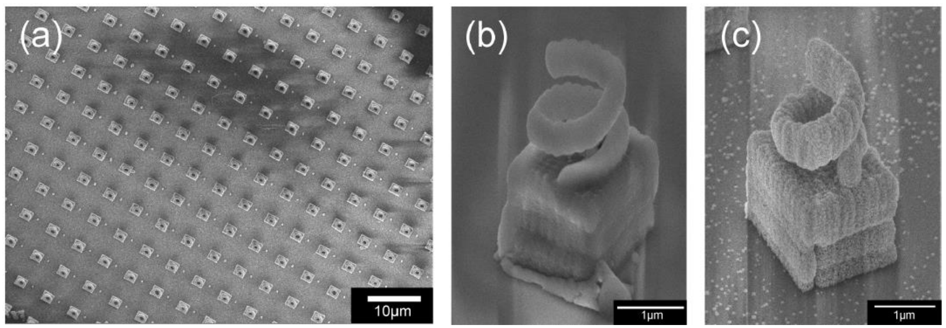
Optical metamaterials

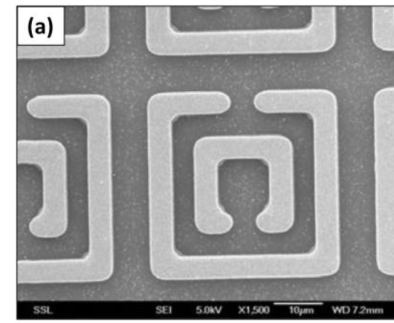
Manufacturing routes:

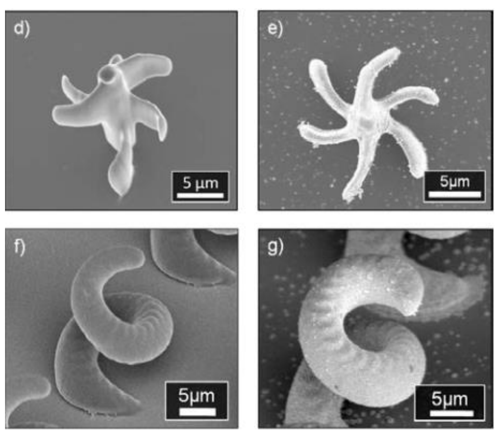
- Two-photon polymerization + metal coating
- Photopolymerization & photoreduction simultaneously

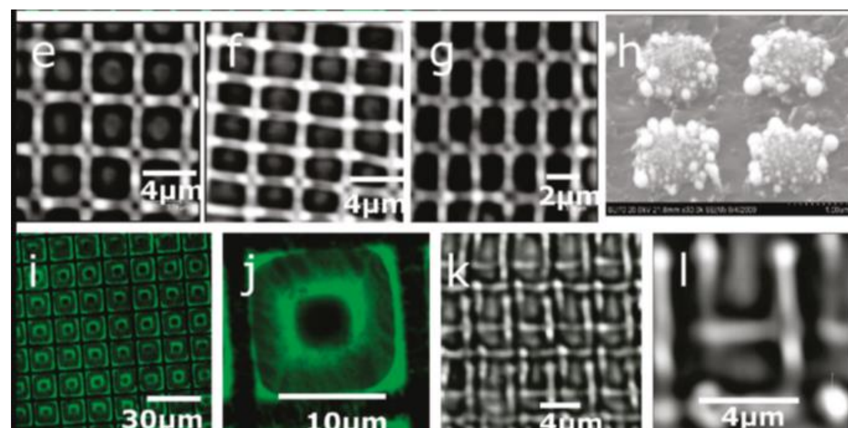


Perfect absorber





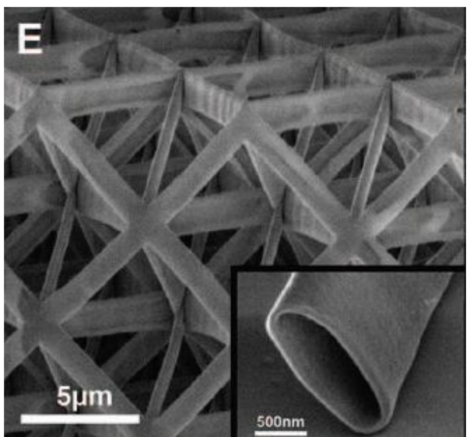


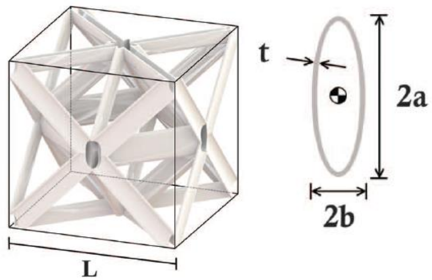


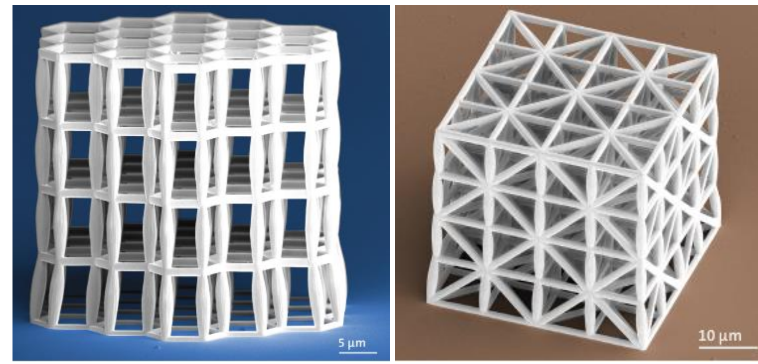
Phy Rev B 88 (2013) 115105; Adv Mater 25 (2013) 3994; IEICE Electronics Express 9 (2012) 34;
Opt Mater Exp 1 (2011) 1548; Acs Nano 5 (2011) 1947

Mechanical metamaterials

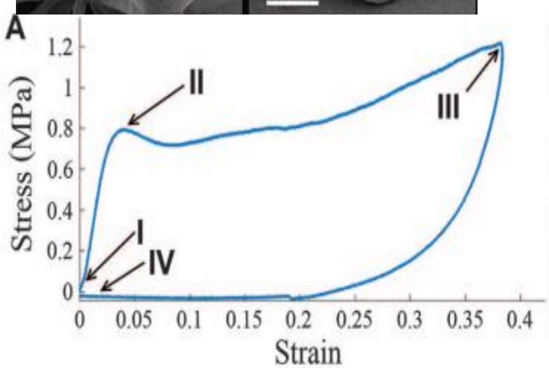
- Artificial structures with mechanical properties defined by structures rather than their composition
- Nanolattice: strong & lightweight

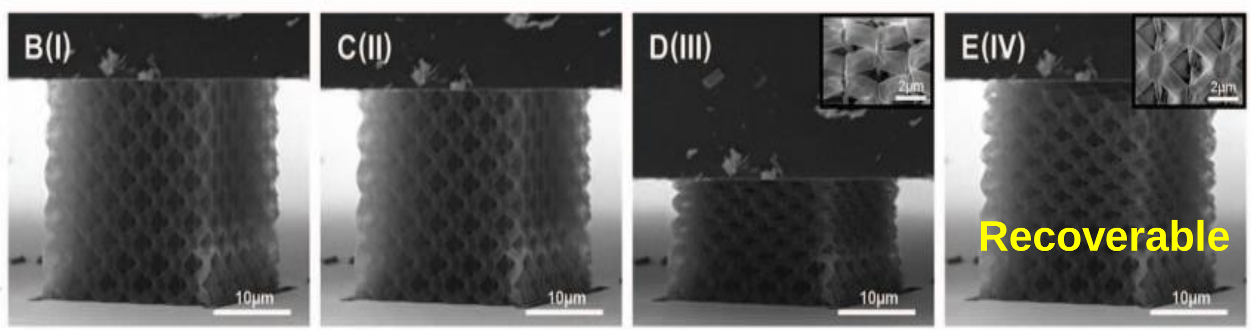






Strength up to 280 MPa!





L = 5 µm; a = 650 nm; t = 10 nm

Science 345 (2014) 1322; PNAS 111 (2014) 2453

Applications:

For fun…

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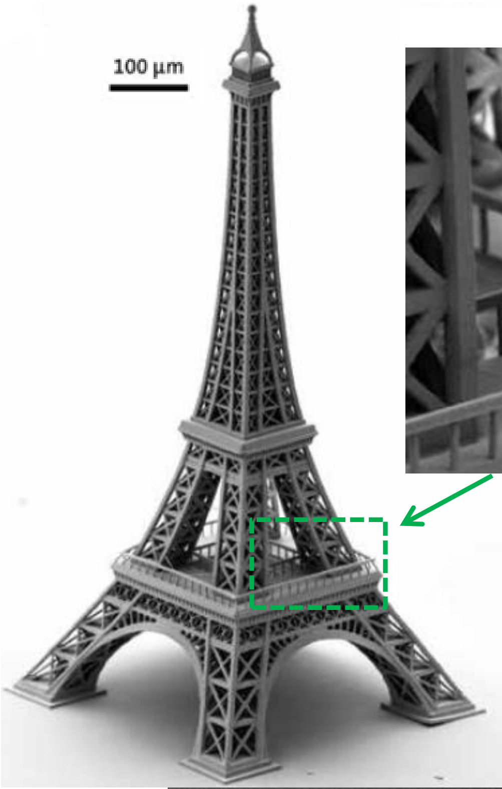

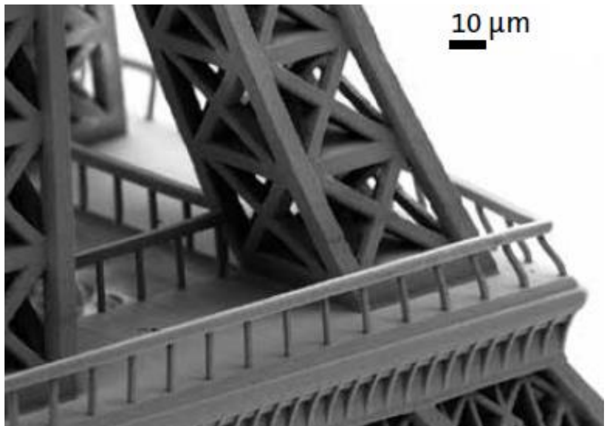

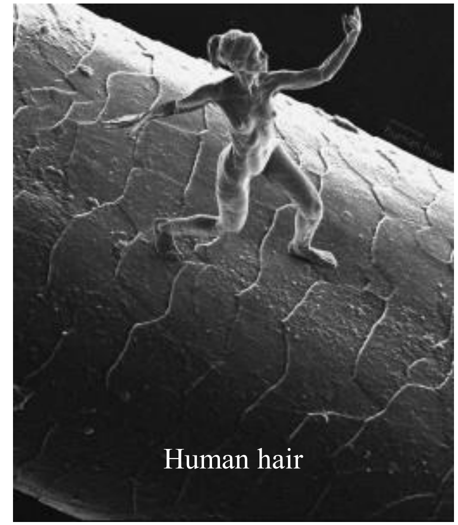

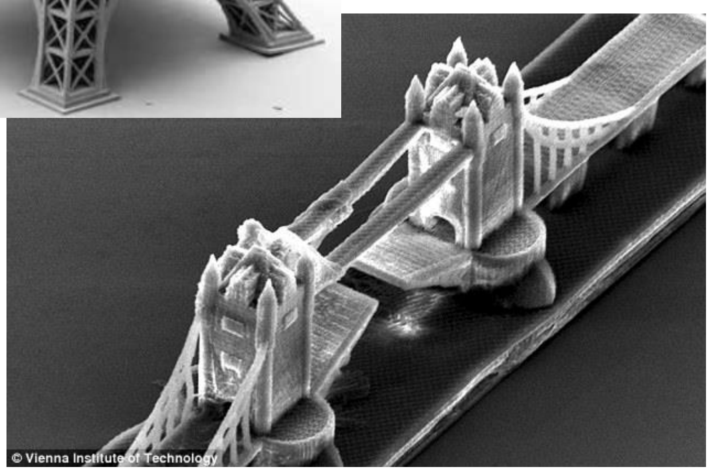

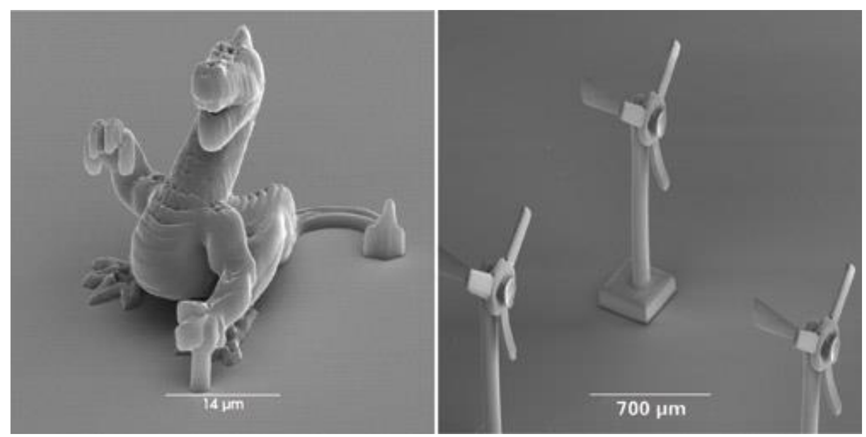

Nanoscribe, Karlsruhe Institute of Technology, Vienna Institute of Technology, Jonty Hurwitz

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Send your questions to Dr Qin Hu

qin.hu@nottingham.ac.uk

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