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14. ABSTRACT
In this report, we summarized major technical achievements as a result of this ONR YIP grant, including 1) the development of a DMD based micro-stereolithography system for direct-write of CNT nanocomposites, 2) laser micromachining and nanopatterning of nanocomposites, 3) and the development of micro-devices using CNT nanocomposites. We also reported the publications, patents, and people developments supported by this YIP grant.

15. SUBJECT TERMS

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N00014-04-1-0568 Final Project Report

Advanced Laser Manufacturing of Polymeric Nanocomposites

PI: Shaochen Chen, The University of Texas at Austin

1. Technical Achievements:

1.1 Research Motivations:

- Carbon nanotube (CNT) reinforced nanocomposites have been proven of excellent mechanical, thermal, electrical, and optical properties. Rapid prototyping of nanocomposite part will have significant impact to US Navy.
- Advanced manufacturing processes are key to the successful applications of CNT-reinforced nanocomposites.
- Lasers are excellent tools for manufacturing, yet little work has been done on advanced laser manufacturing of CNT nanocomposites.

1.2 Research Objectives

- Develop a new, general-purpose micro-stereolithographic method (Flash-μSL) for rapid prototyping of microstructures made of CNT-reinforced nanocomposites.
- Investigate the Ultrafast Laser Ablation (ULA) process of CNT-nanocomposites.
- Develop novel micro/meso-devices using CNT-nanocomposites.

1.3 Research Approaches

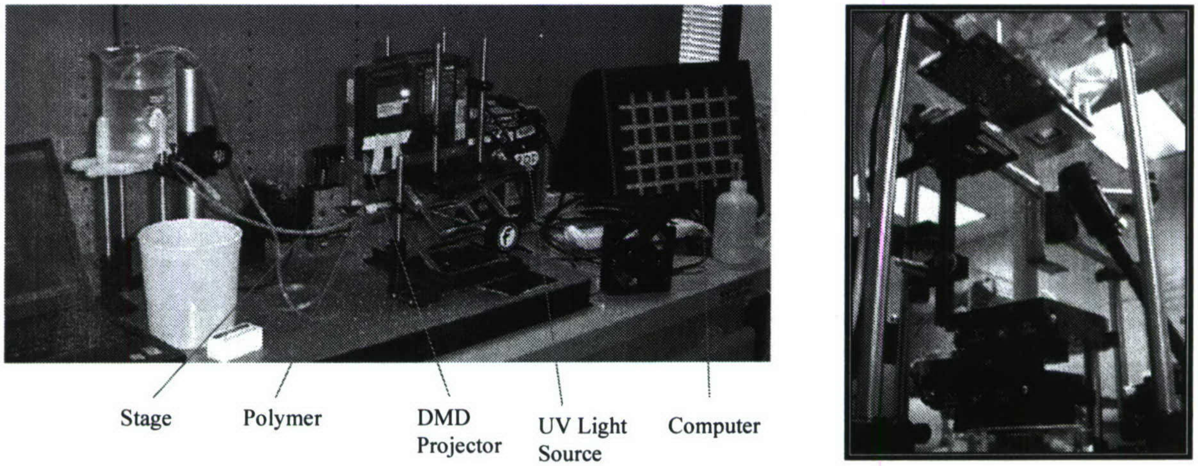
- Use a digital micro-mirror device (DMD) as a dynamic optical mask for the rapid projection of UV light to cure photosensitive polymers for the manufacture of 3-D structures.
- Use both nanosecond and femtosecond pulsed lasers for micro and nano-machining of polymeric nanocomposites.
- Use the Flash-μSL system to produce 3-D devices such as a micro-turbine and scaffolds.

1.4 Research Results

1.4.1 Development of the Flash-μSL system

We have developed two generations of Flash-μSL systems using DMD as the light mask for projection photo-polymerization. The first generation DMD μSL system is schematically shown in **Fig. 1a**. The system consists of five major components: a DMD chip embedded in the projector as a dynamic mask, a light source, a projection lens assembly, a translation stage with a micrometer, and a vat containing macromer solution. All the components cooperate to ensure correct exposure, resolution, and layer thickness. The light was guided through a ¼ inch (6.35 mm) liquid-filled fiber optics. Two bi-convex lenses (18 mm diameter, 40 mm focal length) with 5 mm spacing were used to converge the light emanating from the fiber optics. The projection lens assembly with adjustable aperture and focus consisted of two equal plano-convex lenses (25 mm diameter, 25 mm focal length). Each lens was oriented with the convex surface towards the longer conjugate distance. The aperture was placed in-between two lenses. All lenses were made of UV grade fused silica (Edmund Optics, Barrington, NJ). The average exposure intensity was determined to be 2 mW/cm^2 [Lu, Mapili, Chen, and Roy, 2006, J. Biomedical Materials Research, 77A (2), 396-405].

The second generation of the Flash-μSL system used a DMD tool kit (Discovery 1100, Texas Instruments) for better UV transmission (**Fig. 1b**). The Flash-μSL is coupled with several syringe pumps for delivering multi-solutions for producing heterogeneous 3D microstructures [Han, Mapili, Chen, Roy, Journal of Manufacturing Science and Engineering, in press].



(a) (b)

Fig. 1 *The Flash-μSL systems: (a) using a commercially available computer projector for light modulation; (b) using Texas Instruments' DMD tool kit for higher UV transmission.*

Numerical Simulation: Photo-initiated radical polymerization can be described by the following reaction sequence:

$$S \xrightarrow{h\nu, k_{i1}} R\cdot \tag{1}$$

$$R\cdot + M \xrightarrow{k_{i2}} RM\cdot \tag{2}$$

$$RM\cdot + M \xrightarrow{k_p} RM_2\cdot \tag{3}$$

$$\downarrow$$

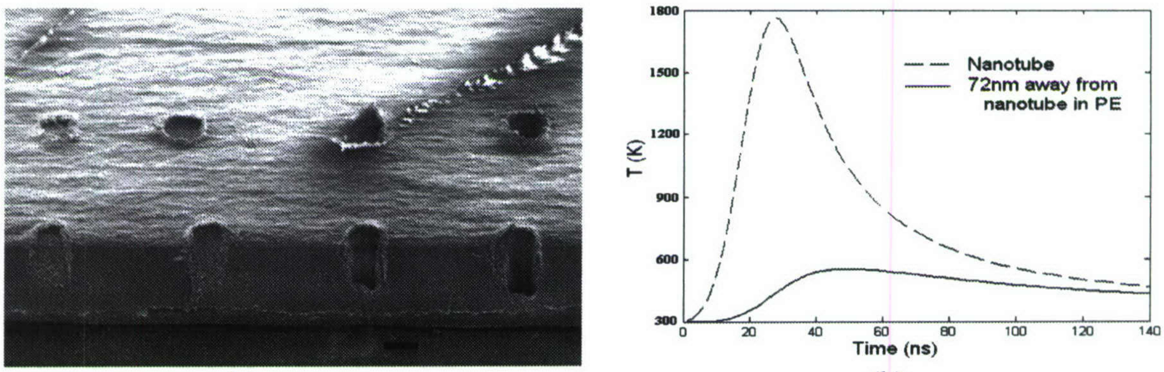
$$RM_{n-1}\cdot + M \xrightarrow{k_p} RM_n\cdot \tag{4}$$

$$RM_{m1}\cdot + RM_n\cdot \xrightarrow{k_t} RM_{m+n}R \tag{5}$$

where S stands for the initiator, R for the radical, M for the monomer, k_{i1} for the rate of generation of primary radical, k_{i2} for the rate of generation of macro radical, k_p for the propagation rate constant, k_t for the radical combination rate constant assuming bi-molecular combination. We have developed numerical models to simulate the photo-polymerization process. Results from the simulation have been used to guide the experimental design [Lu, 2006, UT-Austin Dissertation].

1.4.2 Laser Ablation and Patterning of Nanocomposites

Nanoparticle-Enhanced Laser Micromachining: Polyethylene (PE) is transparent to a UV or visible laser beam and thus it is hard to ablate (machine) pristine PE by lasers. We have demonstrated that by adding a small amount of carbon nanofibers to the PE matrix, we can easily ablate the PE nanocomposite (**Fig. 2a**). The nanofibers serve as "nano-receivers" of the laser energy and then convert the photon energy into heat ("nano-heaters"). Numerical heat conduction simulation (**Fig. 2b**) shown the PE matrix was partially melted or evaporated, due to pyrolytic decomposition [Lu, Shao, Chen, 2005, Transactions of the North American Manufacturing Research Institute of SME, Vol. 33, pp. 243-249].



(a) (b)

Fig. 2 (a) Laser ablated polyethylene nanocomposite. The laser energy used for ablation is much lower due to nano-fiber enhanced absorption. (b) Numerical simulation of heat conduction of the nanofiber and its surrounding polymer matrix.

To control the spatial resolution for nanomanufacturing, we investigated laser nanosphere lithography for glass and semiconductors. We first deposited a monolayer of silica nanospheres on the sample. Then we used a femtosecond laser to illuminate the material. Due to optical near-field effects, the laser beam is "focused" by each nanosphere, thus creating a nanoscale high-intensity laser spot array for nanostructuring. **Fig. 3a** shows the numerical simulation result of the enhanced laser energy after focusing by the nanosphere on glass. **Fig. 3b** shows a 200-nm hole array was produced on the glass [Heltzel, Battula, Howell, Chen, 2007, *Journal of Heat Transfer*, Vol. 129 (no.1), pp.53-59].

(a) (b)

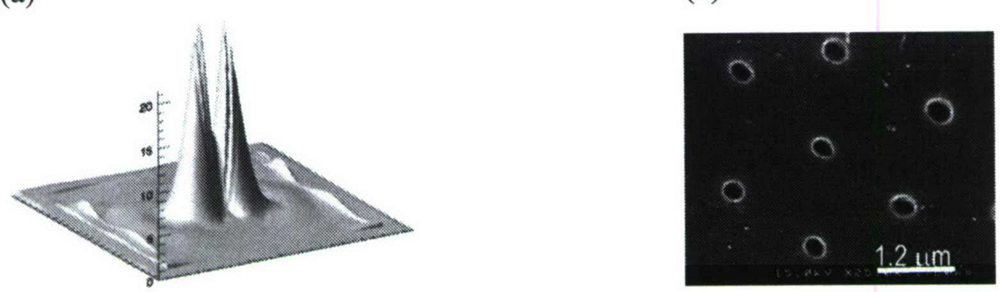


Fig. 3 (a) Numerical simulation using finite difference time domain method shows strong laser intensity enhancement due to the nanosphere; (b) experimental demonstration shows a 200-nm hole array was produced on glass.

Nanoparticle-Enhanced Laser Micro/Nano-Imprinting: We have developed a laser nanoimprinting process for micro/nano-patterning of polymeric nanocomposites. The process involves selective heating the nanoparticles by laser to soften the composite and then molding the sample using a quartz mold (**Fig. 4a**). This is a highly parallel process to fabricating devices made of nanocomposites with excellent thermal / mechanical / optical / electrical properties (**Fig. 4b**) [Lu, Shao, Chen, 2004, Applied Physics Letters, Vol. 85, no. 9, pp. 1604-1606].

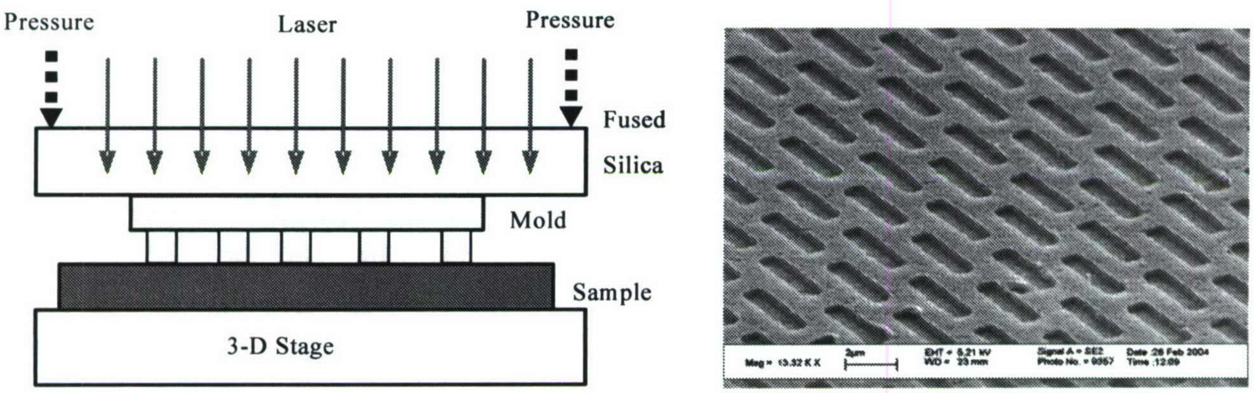
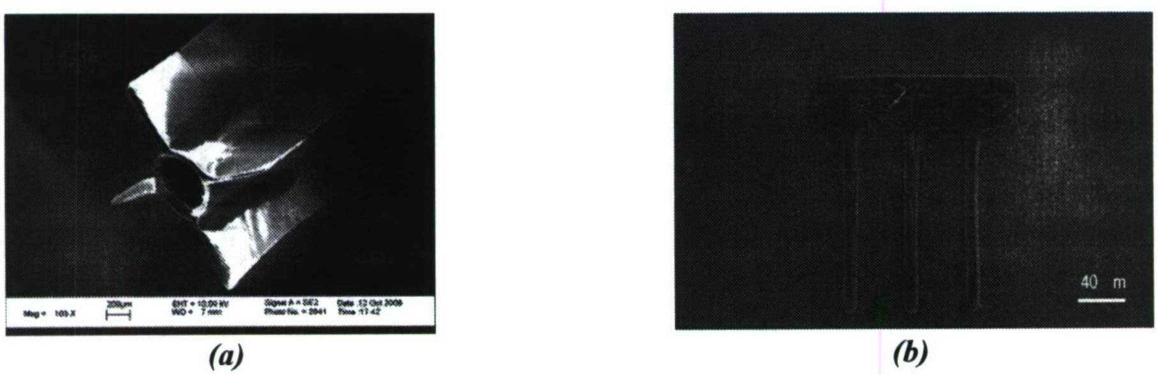


Fig. 4 *(a) Schematic of the laser nano-imprinting processs. (b) Parallel micro/nano-pattern on polyethylene nanocomposite fabricated by laser imprinting.*

1.4.3 Device Applications

Micro-turbine and Micro-actuators: We have demonstrated the concept of employing DMD based μSL to rapidly produce high precision, 3D microstructures comprised of single-wall carbon nanotubes (SWNTs) and a photo-curable polymer, 1,6-hexanedioldiacrylate (HDDA). **Fig. 5a** shows a micro-turbine with 4 wings. **Fig. 5b** shows a micro-cantilever with 3 beams directly written by the projection stereolithography method. Our results demonstrate that we can fabricate 3-D micro-devices of nanocomposite materials with various concentrations of SWNTs.



(a) ***(b)***

Fig. 5. ***(a)*** *A micro-turbine fabricated by DMD based μSL,* ***(b)*** *bird's eye view of 3-D micro-cantilever comprised of 0.1% SWNTs and HDDA.*

3D Scaffolds: DMD based μSL has also been used to produce micro-scaffolds that can be used for tissue engineering (**Fig. 6**). The unique feature of the projection printing allows one to encapsulate live cells in the scaffold for organ (e.g. bone or cartilage) development [Lu, Mapili, Chen, and Roy, 2006, J. Biomedical Materials Research, 77A (2), 396-405; Han, Mapili, Chen, Roy, Journal of Manufacturing Science and Engineering, in press].

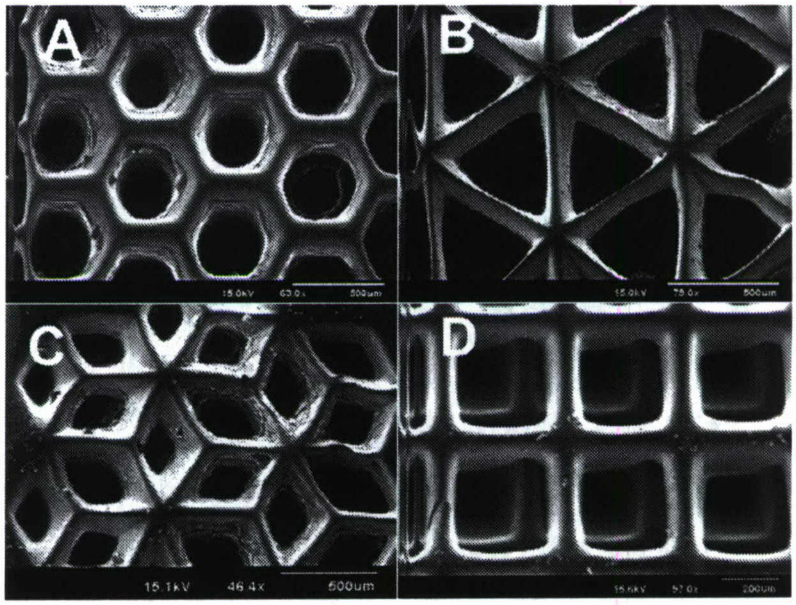


***Fig. 6**. Various shapes of polymer microstructures produced by DMD based μSL: **(a)** circular, **(b)** triangular, **(c)** diamond, and **(d)** square holes (multilayer).*

Direct-write of Microlens Array: We have demonstrated the fabrication of microlens array through projection photopolymerization using the DMD as a dynamic photomask. The DMD projects grayscale images, which are designed in a computer, onto a photo-curable resin. The resin is then solidified with its thickness determined by a grayscale ultraviolet light and exposure time. Therefore various geometries can be formed in a single-step, massively parallel fashion (**Fig. 7**). The physical and optical characteristics of the resulting lenses suggest that this fabrication technique is potentially suitable for applications in integrated optics [Lu and Chen, Applied Physics Letters, accepted]

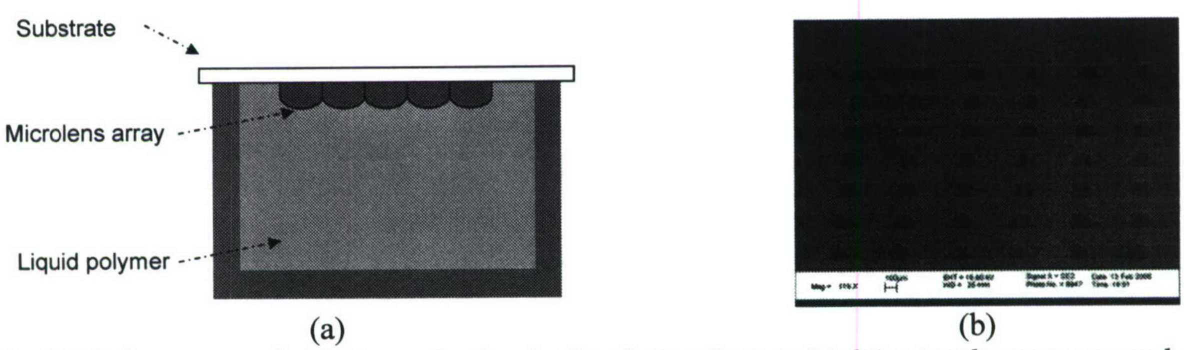


***Fig. 7** (a) the gray-scale photo-projection in the photopolymer; (right) microlens array produced by one exposure fabricated by μSL.*

2. People and Leadership Development:

The YIP grant (2004-2007) has been a significant support to the following people/leadership development:

- **The PI, Prof. Shaochen Chen**
  - Promoted to Associate Professor with tenure in 2005,
  - Received Outstanding Faculty Award, College of Engineering, UT in 2005,
  - Received P.D. Henderson Centennial Endowed Faculty Fellowship, UT in 2006,
  - Became Associate Editor, *Journal of Biomedical Nanotechnology* in 2007,
  - Became Associate Editor, *Journal of Manufacturing Science & Engineering* in 2007,
  - Elected Fellow of American Society of Mechanical Engineers (ASME) in 2007,
  - Gave invited talks/seminars in Naval Research Lab, IBM T.J. Watson Research Center, and 30 universities including: MIT, UC Berkeley, Stanford, Princeton, Carnegie Mellon Univ, Northwestern Univ, Georgia Tech, UCLA, UCSD, USC.

- **Graduate Students**
  - **Yi Lu**: received his PhD in 2006 with a research topic in DMD based laser stereolithography of polymers and nanocomposites.
  - **Arvind Battula**: received his PhD in 2007 with a research topic in femtosecond laser nanofabrication and nanophotonics.
  - **Li-Hsin Han**: to receive his PhD in 2008 (expected) with a research topic in stereolithography of heterogeneous micro and nanostructures and devices.
  - **Carlos Aguilar**: A minority student who received his MS in 2005 with research topic in laser processing of biopolymers. Carlos is continuing his PhD in Dr. Chen's group.

- **Graduate Student Awards:**
  - **Carlos Aguilar**
    - Continuing Fellowship, UT-Austin, 2007-2008
    - George H. Mitchell Award for Excellence in Graduate Research, 2007 (three recipients university-wide per year)
    - Nomination for George H. Mitchell Award for Excellence in Graduate Research, 2005
    - University of Texas - College of Engineering Graduate Fellowship: 2004, 2005
    - Hispanic Engineering National Awards Annual Conference Scholar, 2004, 2005, 2006
    - General Motors Foundation Scholar, 2004, 2005, 2006
    - Founder & Co-President, Engineers Without Borders
    - Co-Founder, Engineers for Sustainable World
    - Member & Graduate Representative, Tau Beta Pi
    - Member & Graduate Representative, Society of Hispanic Professional Engineers
  - **Li-Hsin Han**
    - Continuing Fellowship, UT-Austin, 2006-2007
    - Three patents were awarded to Leo for his work in catheter probe for cardiovascular imaging

- **Yi Lu**
  - Outstanding Thesis Award, University of Texas at Austin, 2004 (four recipients university-wide per year)

- **Undergraduate Student Researchers:** The following undergraduate students have been involved in the YIP projects to gain research experience:

- Brandon Beberwyck (5/07- present)	- Jennifer Tobias (4/06-8/06)
- Chris Javadi (5/06-12/06)	- Darren Cooper (4/06-8/06)
- Gerry Suhali (5/05-5/06)	- Aaron Hulse (9/03-5/04)

3. Patents:

Five patents/provisional patents were developed as a result of this YIP grant. Three were licensed to CardioSpectra Inc. (CSI, a VC founded startup company). CSI is in the process of being purchased by a public company.

- "Catheter Imaging Probe and Method", M. D. Feldman, T. E. Milner, S. C. Chen, J. H. Kim, L. H. Han, J.-H. Oh, H. Lee. US and International patent filed in 2003 and 2004. US Provisional Patent Application Serial No. 60/466,215. The patent was licensed to CardioSpectra, Inc. in 2005.
- "Optical Coherence Tomography Using Spectrally Resolved Bandwidth", M. D. Feldman, T. E. Milner, J.-H. Oh, E. Kim, K. Kumar, C. Condit, R. Grant, N. Kemp, J. H. Kim, S. C. Chen, L. H. Han, US Provisional Patent Application Serial No. 60/687,930. The patent was licensed to CardioSpectra, Inc. in 2005.
- "Rotating Optical Catheter Tip for Optical Coherence Tomography", T. E. Milner, M. D. Feldman, J.-H. Oh, S. C. Chen, US Provisional Patent Application Serial No. 11/551,684, 2006. The patent was licensed to CardioSpectra, Inc. in 2006.
- "A Device and Method for Rapid Fabrication of Multi-material, 3-dimensional Microstructures", L.H. Han, G. Mapili, S.C. Chen, and K. Roy, US Provisional Patent Application Serial No. 60/952595, 2007.
- "Direct Forming of Micro-optics Using Dynamic Photomask" Y. Lu and S.C. Chen, US Provisional Patent Application in preparation, 2007.

4. Publications:

The following publications are the results of the YIP grant:

4.1 Peer-reviewed Journal Publications:

1. Y. Lu, S. C. Chen, "Direct-write of Microlens Array Using Digital Projection Photopolymerization", *Applied Physics Letters*, accepted.
2. L. H. Han, G. Mapili, S.C. Chen, K. Roy, "Projection Micro-Fabrication of Three-Dimensional Scaffolds for Tissue Engineering", *Journal of Manufacturing Science and Engineering*, in press.
3. K. C. Dickey, S. Subramanian, J. E. Anthony, L. H. Han, S.C. Chen, and Y.L. Loo, "Large-area patterning of a solution-processable organic semiconductor to reduce parasitic leakage and off currents in thin-film transistors", *Applied Physics Letters*, Vol. 90, 244103, 2007.

4. A. J. Heltzel, A. Battula, J. R. Howell, S. C. Chen, "Nanostructuring Borosilicate Glass with Near-field Enhanced Energy Using a Femtosecond Laser Pulse", *Journal of Heat Transfer*, Vol. 129 (no.1), pp.53-59, 2007.
5. D.B. Shao, S.C. Chen, "Direct Patterning of Three-dimensional Periodic Nanostructures by Surface Plasmon Assisted Nanolithography", *Nano Letters*, Vol. 6 (10), pp. 2279-2283, 2006.
6. N. Gomez, Y. Lu, S.C. Chen, C. Schmidt, "Immobilized Nerve Growth Factor and Microtopography Have Distinct Effects on Polarization Versus Axon Elongation in Hippocampal Cells in Culture", *Biomaterials*, Vol. 28 (2), pp. 271-284, 2006.
7. L.H. Han, T.J. Tang, S.C. Chen, "Turning the Absorption of Au Nanospheres on a Micro-Shell by Photo-Deformation", *Nanotechnology*, Vol. 17, pp.4600-4605, 2006.
8. Y. Lu, G. Mapili, G. Suhali, S.C. Chen, K. Roy, "A Digital Micro-mirror Device (DMD)-based System for the microfabrication of Complex, Spatially Patterned Tissue Engineering Scaffolds", *Journal of Biomedical Materials Research A,* Vol. 77A (2), pp 396-405, 2006.
9. A. Battula, S. Theppakuttai, S. C. Chen, "Direct Parallel Nano-patterning of SiC by Laser Nanosphere Lithography", *Journal of Microlithography, Microfabrication, and Microsystems*, Vol.5 (1), pp. 011009, 2006.
10. C. A. Aguilar, Y. Lu, S. Mao, S.C. Chen, "Micro-patterning of Biodegradable Polymers Using Ultraviolet and Femtosecond Lasers", *Biomaterials*, Vol. 26 (36), pp. 7642-7649, 2005.
11. G. Mapili, Y. Lu, S.C. Chen, K. Roy, "Laser-layered Micro-fabrication of Spatially Patterned, Functionalized Tissue Engineering Scaffolds", *Journal of Biomedical Materials Research B,* Vol. 75B (2), pp. 414-424, 2005.
12. Y. Lu, C. A. Aguilar, S.C. Chen, "Shaping Biodegradable Polymers as Nanostructures: Fabrication and Applications", *Drug Discovery Today*, Vol. 2 (1), pp. 97-102, 2005.
13. Y. Lu, D.B. Shao, S. C. Chen, "Nanoparticle-enhanced Laser Micromachining of Nanocomposites", *Transactions of the North American Manufacturing Research Institute of SME,* Vol. 33, pp. 243-249, 2005.
14. D.B. Shao, S. F. Li, S.C. Chen, "Near-field-enhanced, Mold-assisted, Parallel Direct Nanostructuring of a Gold Thin Film on Glass", *Applied Physics Letters*, Vol. 85 (22), pp. 5346-5348, 2004.
15. Y. Lu, D. B. Shao, S. C. Chen, "Laser-assisted Photothermal Imprinting of Nanocomposites", *Applied Physics Letters*, Vol. 85 (9), pp.1604-1606, 2004.

4.2 Peer-reviewed Publications in Conference Proceedings:

1. L. H. Han, G. Mapili, S.C. Chen, K. Roy, "Freeform Fabrication of Biological Scaffolds by Projection Photopolymerization", *Proceedings of the Eighteenth Solid Freeform Fabrication Symposium*, Austin, 2007.
2. D.B. Shao, S.C. Chen, "Surface Plasmons-Assisted Laser Nanolithography Using Metallic Masks", *International Symposium of Nanomanufacturing*, MIT, Boston, 2006.
3. S.C. Chen, "A Digital Micro-mirror Device (DMD)-based System for the Microfabrication of Complex, Spatially Patterned Tissue Engineering Scaffolds,", *Proceedings of 2006 National Science Foundation DMII Grantees Conference*, Saint Louis, 2006.

4. A.R. Battula, S. C. Chen, "Laser-Nanostructure Interactions and Applications for Parallel Nanomanufacturing", *Proceedings of SPIE-the International Society for Optical Engineering,* 2006 (**invited**)
5. A.R. Battula, S. Theppakuttai, S.C. Chen, "Nanosphere-Assisted Direct-patterning of Silicon Carbide by a Nanosecond Pulsed Laser", *2005 ASME International Mechanical Engineering Congress and Exposition*, Orlando, Florida.
6. D.B. Shao, S.C. Chen, "Nanoscale Photolithography Using Surface Plasmons", *2005 ASME International Mechanical Engineering Congress and Exposition*, Orlando, Florida.
7. A.R. Battula, S. Theppakuttai, S.C. Chen, "Nanosphere-Assisted Direct-patterning of Silicon Carbide by a Nanosecond Pulsed Laser", *International Congress on Applications of Lasers and Electro-Optics,* Florida, 2005.
8. A. Battula, S. Theppakuttai, S. C. Chen, "Multi-photon Effects in Nanomachining of SiC by a Nanosecond Pulsed Laser", *Conference on Laser Ablation*, Banff, Canada, 2005.
9. D.B. Shao, S.C. Chen, "Surface Plasmons-Asisted Nanoscale Photolithography", *ASME Integrated Nanosystems Conference*, Berkeley, 2005.
10. L.H. Han, S.C. Chen, "Photo-deformation of Microshells of Nanometer Thick", *ASME Integrated Nanosystems Conference*, Berkeley, 2005.
11. C. A. Aguilar, Y. Lu, S. C. Chen, "Effect of Pulse Number and Pulse Energy on Surface Micro-Patterning of Biodegradable Polymeric Materials using Femtosecond Lasers", *ASME National Heat Transfer Conference,* San Francisco, 2005.
12. Y. Lu, D. B. Shao, S. C. Chen, "Photothermal Imprinting of Nanocomposites Using Pulsed Laser Heating", *ASME National Heat Transfer Conference,* San Francisco, 2005.
13. C. A. Aguilar, Y. Lu, S. C. Chen, "Direct Micro-patterning of Biodegradable Polymers Using Ultraviolet and Femtosecond Lasers", *Proceedings of 2005 National Science Foundation DMII Grantees Conference*, Scottsdale, Arizona, 2005.
14. C. A. Aguilar, Y. Lu, S. C. Chen, "Fabrication of Biodegradable Polymeric Microdevices Using Pulsed-Laser Micromachining," *Proceedings of 41st Meeting of the Society of Engineering Science*, 2004.
15. Y. Lu, D. B. Shao, S. C. Chen, "Laser-assisted Photothermal Imprinting of Nanocomposite", *Proceedings of the 15th Symposium of Solid Freeform Fabrication,* 2004.

4.3 Book Chapters and Dissertations:

1. A. R. Battula, "*Optical Near-field Effects for Submicron Patterning and Plasmonic Optical Devices*", Dissertation, UT-Austin, 2007.
2. D. A. Fozdar, Y. Lu, D. B. Shao, and S. C. Chen, "Chapter 4: Nano/Micro-fabrication Techniques for Organic Electronics and Photonics", book chapter in *Handbook of Organic Electronics and Photonics* (American Scientific Publishers), 2007.
3. S.C. Chen, C. A. Aguilar, Y. Lu, "Rapid Prototyping", book chapter in *Encyclopedia of Biomaterials and Biomedical Engineering* (Marcel Dekker), 2006.
4. Y. Lu, "*Micro/Nano Fabrication of Polymeric Materials by DMD-based Micro-Stereolithography and Photothermal Imprinting*", Dissertation, Dissertation, UT-Austin, 2006.
5. D. B. Shao, "*Sub-wavelength Optical Phenomena and Their Applications in Nano-fabrication*", Dissertation, UT-Austin, 2006.

6. C.A. Aguilar, "*Direct Micro-Patterning of Biodegradable Polymers Using Ultraviolet and Femtosecond Lasers*", MS Thesis, UT-Austin, 2005.
7. S. C. Chen and Y. Lu, "Chapter 10: Micro and Nano-fabrication of Biodegradable Polymers", book chapter in *Handbook of Biodegradable Polymeric Materials and Their Applications* (American Scientific Publishers), 2004.

URL of Dr. Chen's Research Group: http://www.me.utexas.edu/~scchen/