

Fabrication of Self-organized Metal-Polymer Hybrid Structures for Optics and Photonics

- Biomimetic Photonic Materials Design -

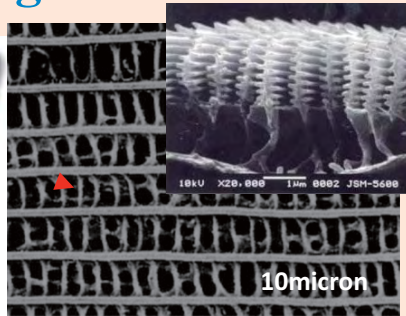
Masatsugu SHIMOMURA, Hiroshi YABU, Daisuke ISHII, and Yuji HIRAI

Institute of Multidisciplinary Research for Advanced Materials
WPI Research Center : Advanced Institute for Materials Research,
Tohoku University
JST-CREST



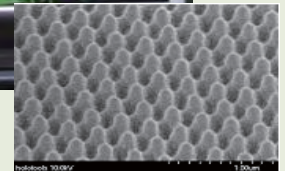
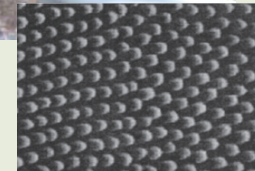
New Generation of Biomimetic Materials

Butterfly wing-scale:structure color



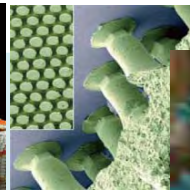
> Fibers, coating, photonics

Moth-eye structure:anti reflectant



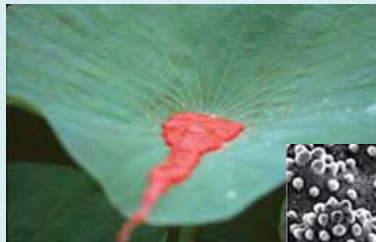
> Anti-reflection film
photonics

Gecko Hand : adhesion



> adhesive

Lotus Effect : hydrophobic



self-cleaning surface

> coating, painting, anti-fogging

Sharkskin : riblet



> Painting, coating.
Anti-fouling

Self-Organized Patterns in Daily Life

Japanische Miso Suppe



Benard convection

Wine Legs



Fingering instability

Coffee Stain



Dewetting phenomenon

Pattern formation by Self-organization



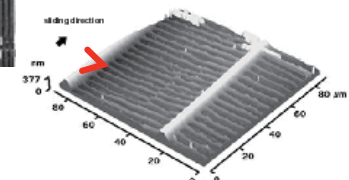
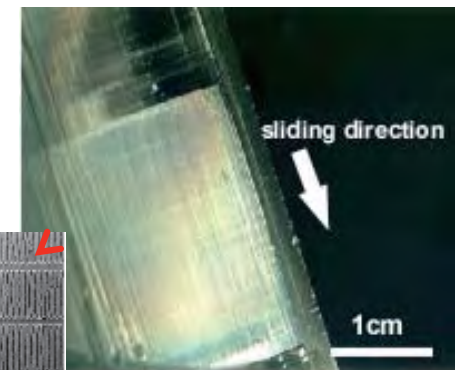
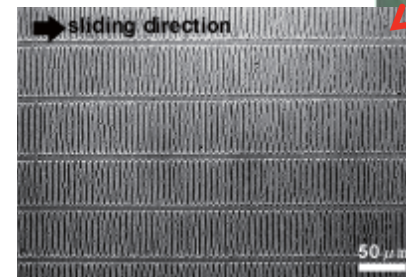
Ilya Prigogine

Dissipative structures
Far from thermal equilibrium

General physical phenomena
for any materials in any scale

Novel Nano Materials

Chem.Lett.,(1996), Supramol.Sci., 5, 331-336 (1998), Chaos (1999),
J.Phys.Soc.Jpn.(2003), Advanced Functional Materials, 15(4), 575-581 (2005).



Self-Organized Patterns in Daily Life



Benard convection



Fingering instability



Coffee Stain



Dewetting phenomenon



Breath figures
(dewetting)



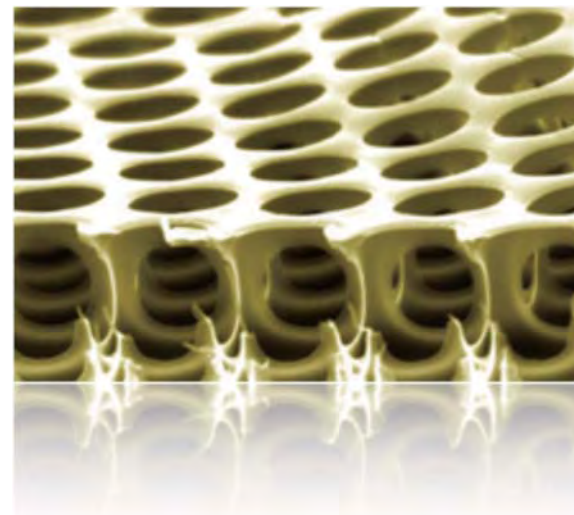
Ilya Prigogine

Pattern formation by Self-organization

Dissipative structures

**General physical phenomena
for any materials in any scale**

Novel Nano Materials



Supramol. Sci., 5, 331-336 (1998), Langmuir, 16 (15), 6071-6076 (2000)

Casting of Polymer Solution under High-Humid Condition

What's happening?



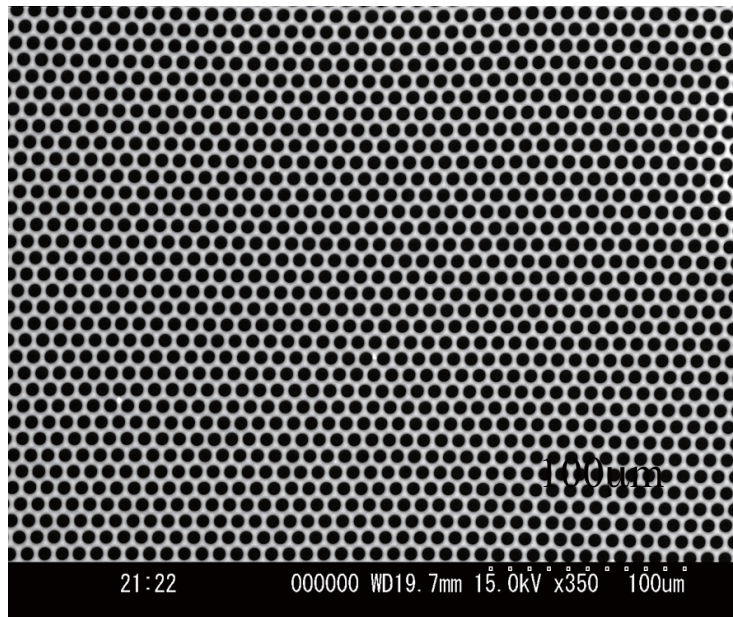
***In-situ* optical microscopy of solution surface during solvent evaporation shows . . .**



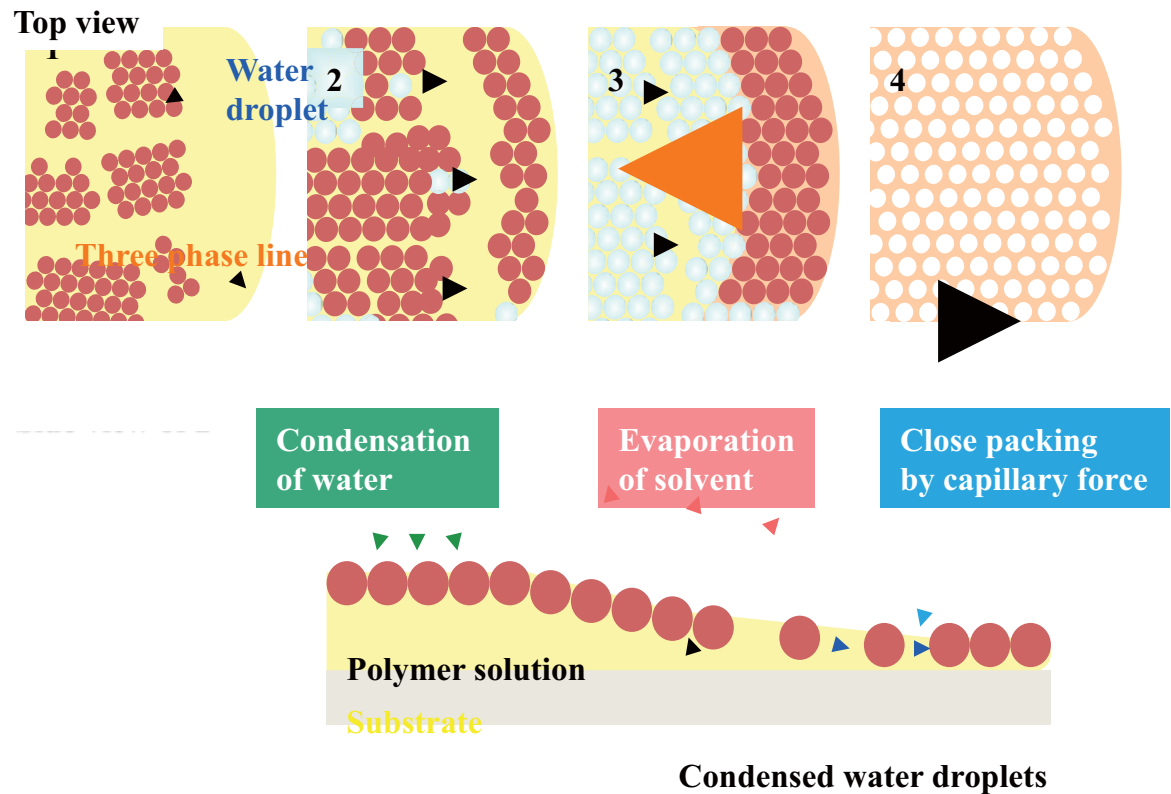
Fabrication of Honeycomb Film on Flat Substrate
(Dr. Ozono)

Honeycomb Patterned Polymer Film Prepared under Humid Condition

a SEM image

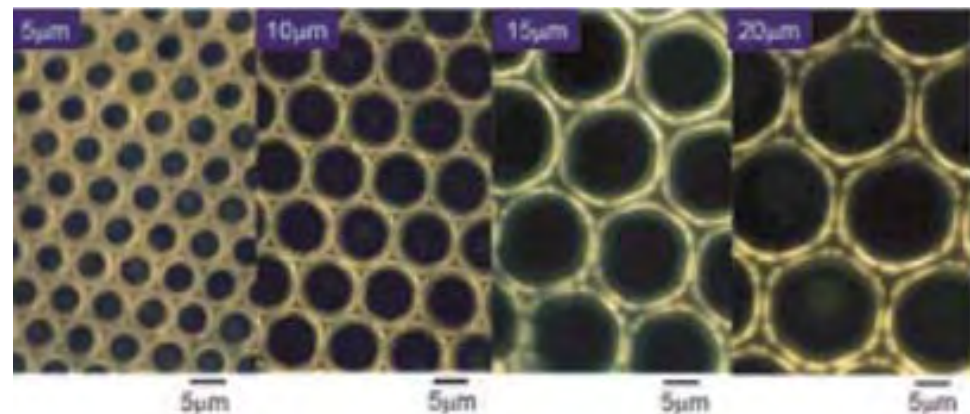
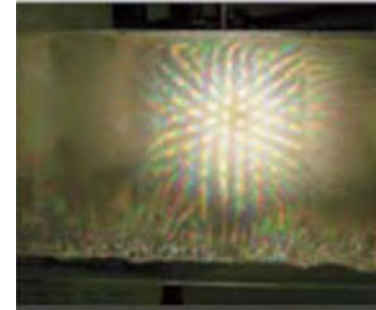
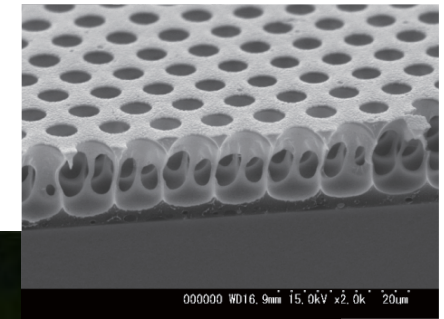


b schematic formation mechanism



water droplets condensed on polymer solution act as template

Small Pilot Plant for Honeycomb Film Fabrication Designed by Fuji Film Co.ltd



Fabrication and Optical Property of Self-Organized Honeycomb-Patterned Films

NOBUHITO KURONO^a, RYOKO SHIMADA^b,
 TERUYA ISHIHARA^a and MASATSUGU SHIMOMURA^{a,c}

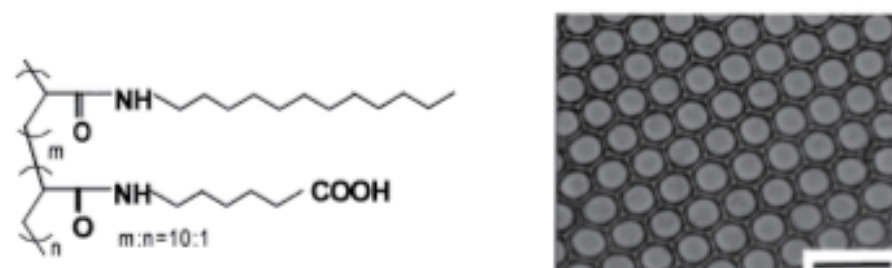


Figure 1. Chemical structure of polyacrylamide derivatives used in this study (left). Optical micrographs of a honeycomb-patterned film. Scale bar: 10 μm (right).

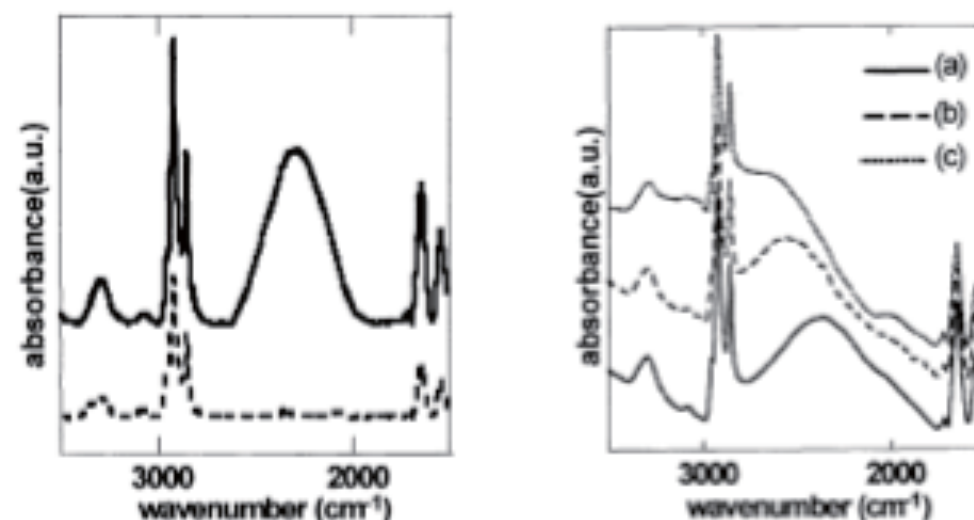
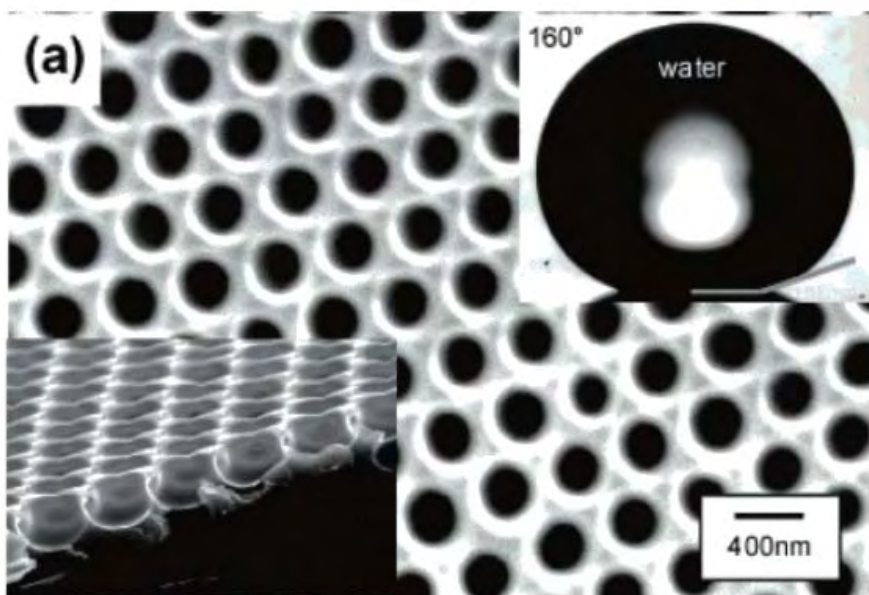
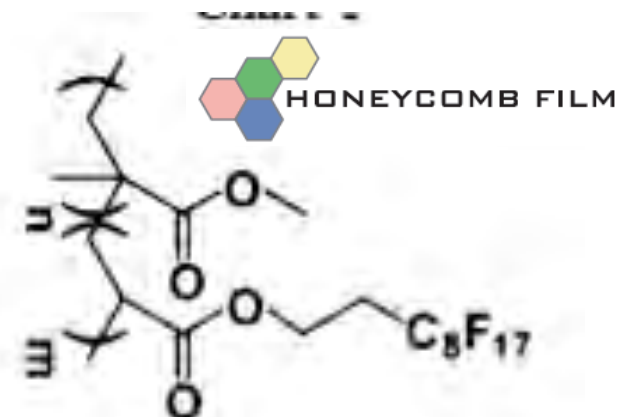


Figure 2.(left) FT-IR spectra of honeycomb-patterned and spin-coated films. solid line: honeycomb-patterned film; dashed line: spin-coated film.

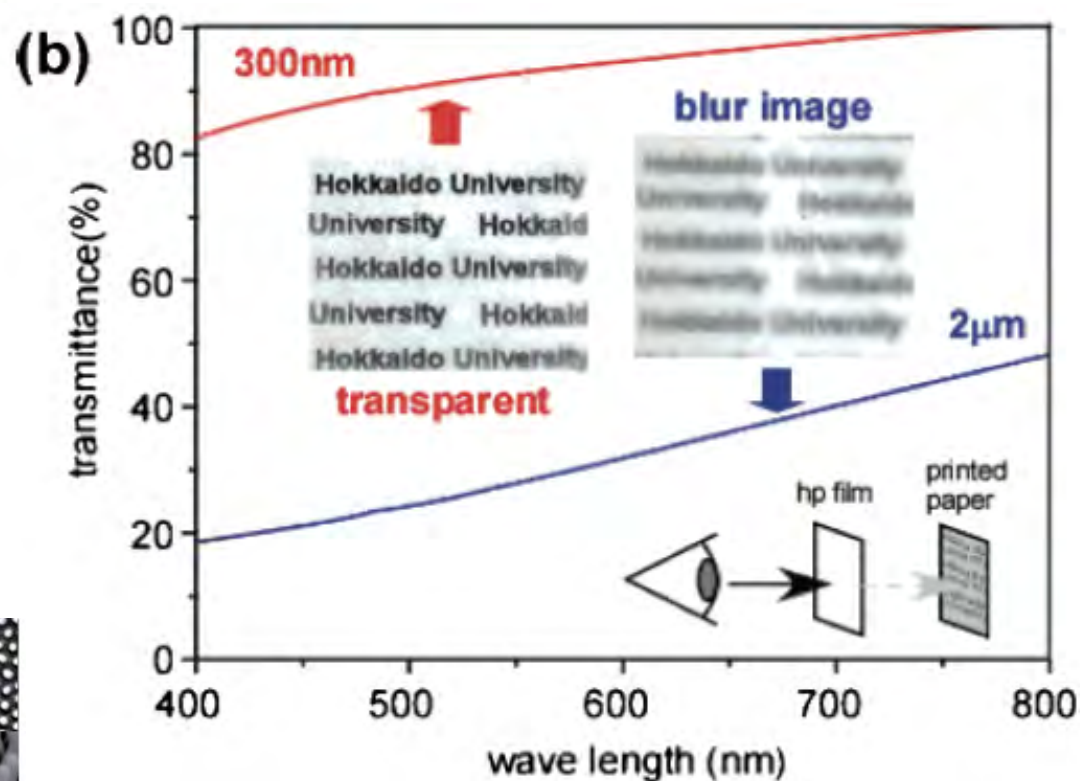
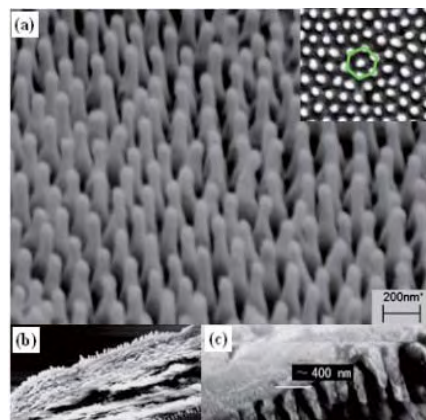
Figure 3.(right) Effect of the pore size of honeycomb-patterned films. Pore sizes of honeycomb-patterned films is about 3.9 (a), 4.1 (b), 4.3 (c) μm, respectively.

Single-Step Fabrication of Transparent Superhydrophobic Porous Polymer Films

Hiroshi Yabu^{†,‡} and Masatsugu Shimomura^{*,†,‡,§}



Cicada wing
Hydrophobic &
Transparent



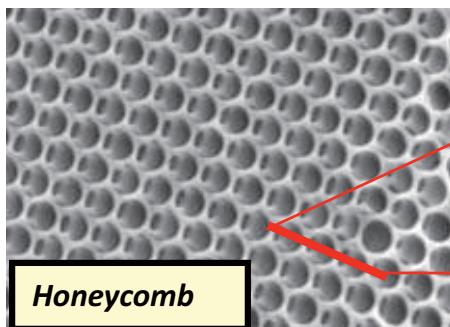
Chem. Mater. 2005, 17, 5231–5234



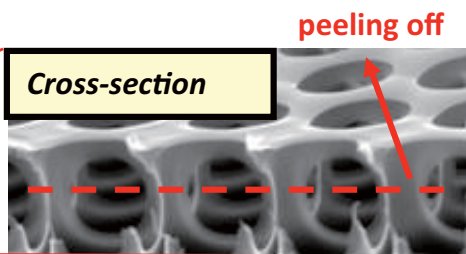
polystyrene



edge width ~50nm

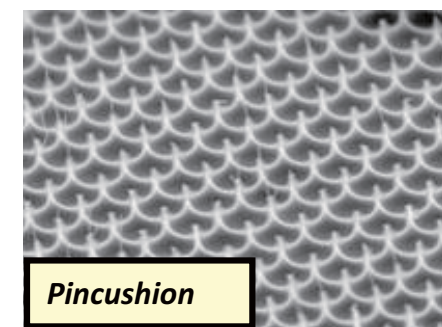


Honeycomb

5 μm 

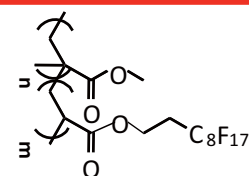
peeling off

Cross-section



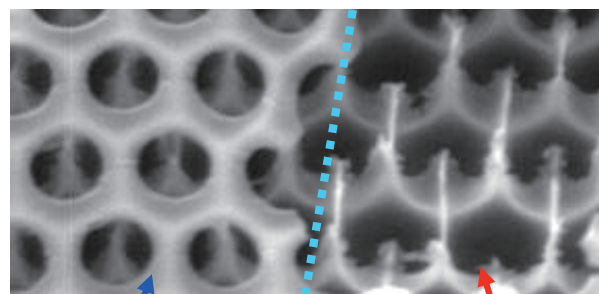
Pincushion

5 μm



1 n:m=1:1

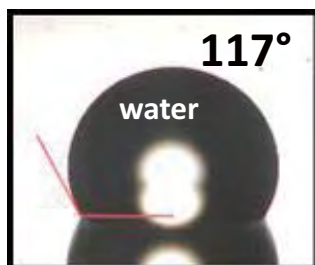
Flat film



Honeycomb

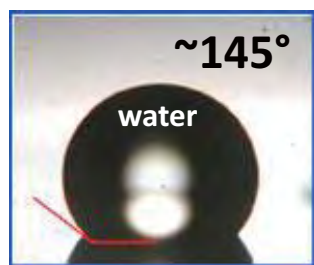
Pincushion

Fabrication of non-wetting surface by using self-organization



117°

water



$\sim 145^\circ$

water



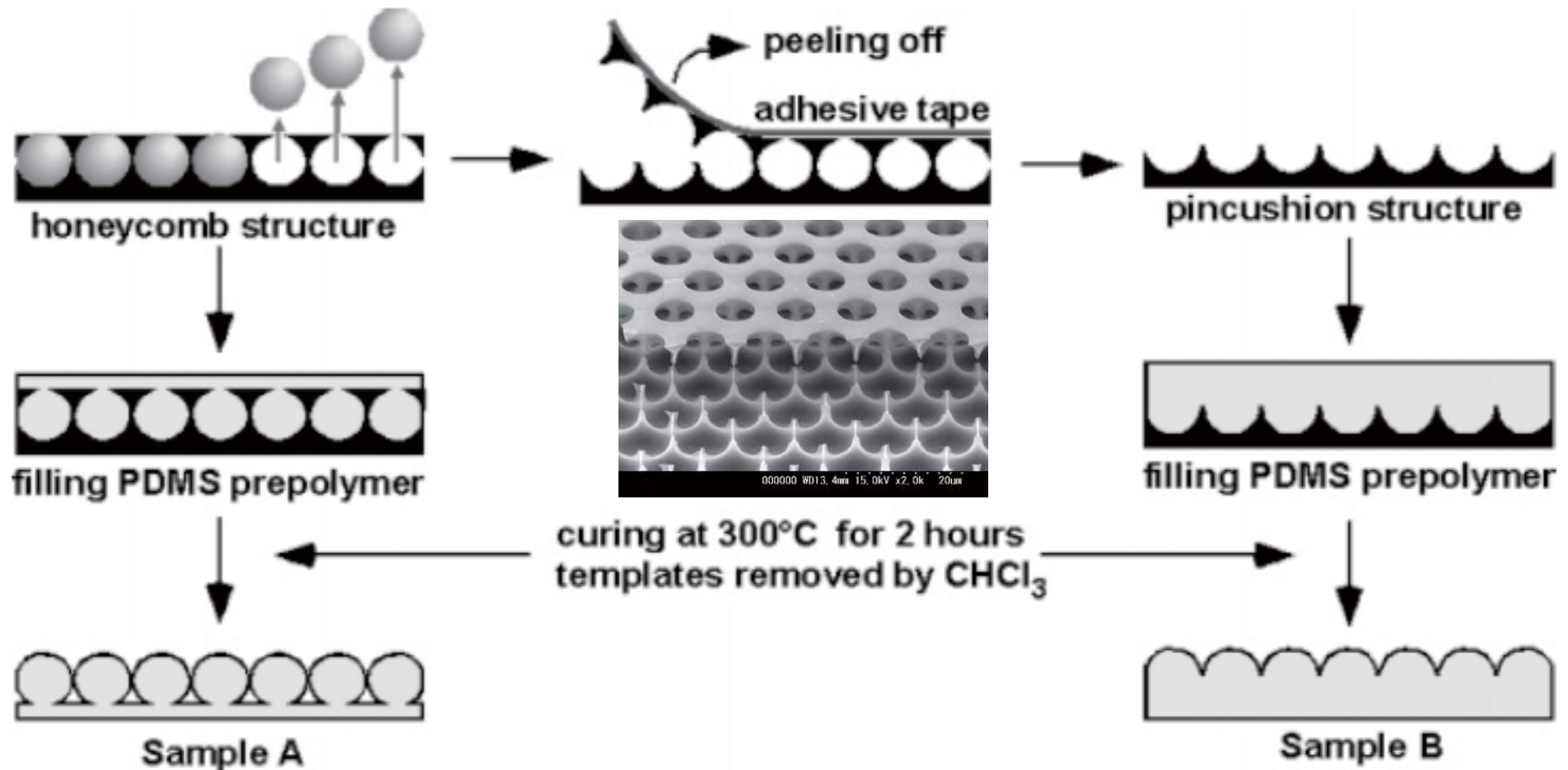
$\sim 170^\circ$

water

*Honeycomb-patterned films and pin-cushion structures prepared by casting $\text{CF}_3\text{CF}_2\text{CHCl}_2/\text{CClF}_2\text{CHClF}$ solution of copolymer **1** on glass substrate. 10 μL of water droplet was placed on each prepared films.*

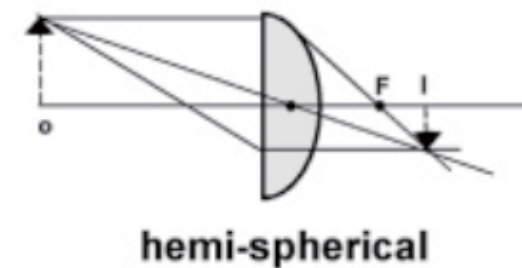
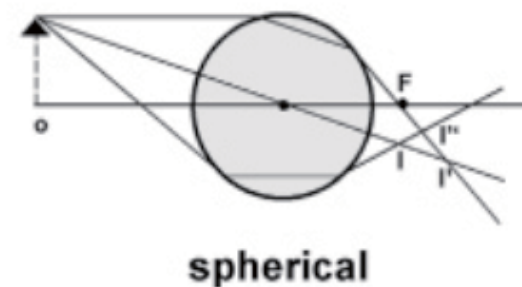
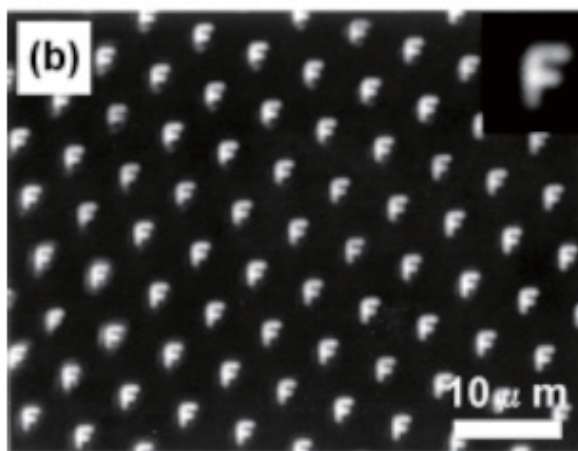
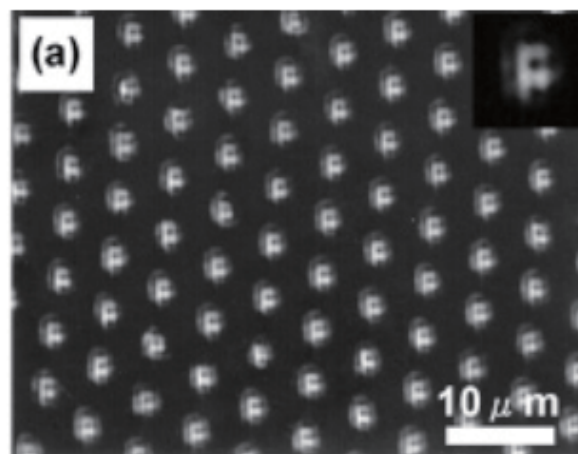
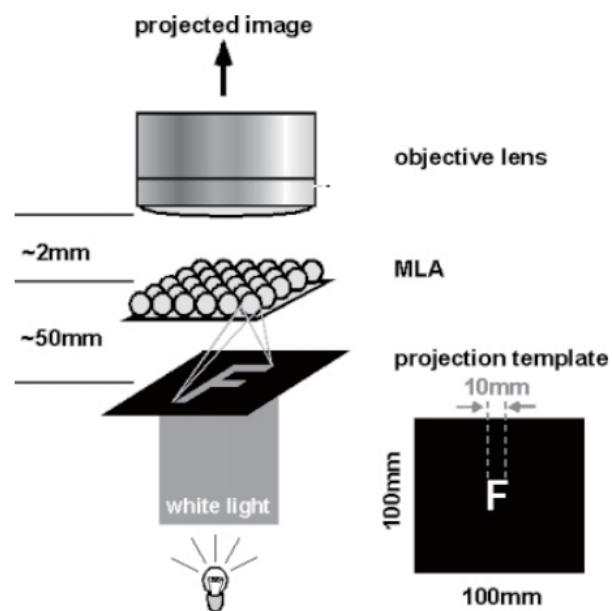
Simple Fabrication of Micro Lens Arrays

Hiroshi Yabu^{*,†,‡,§} and Masatsugu Shimomura^{†,‡,§}



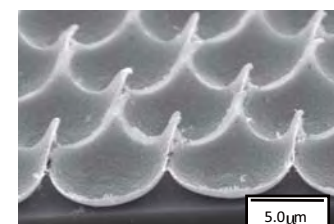
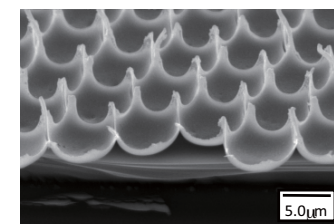
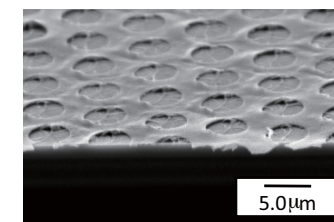
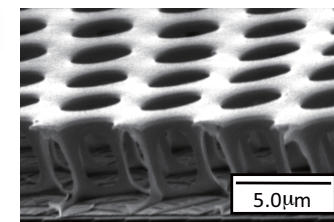
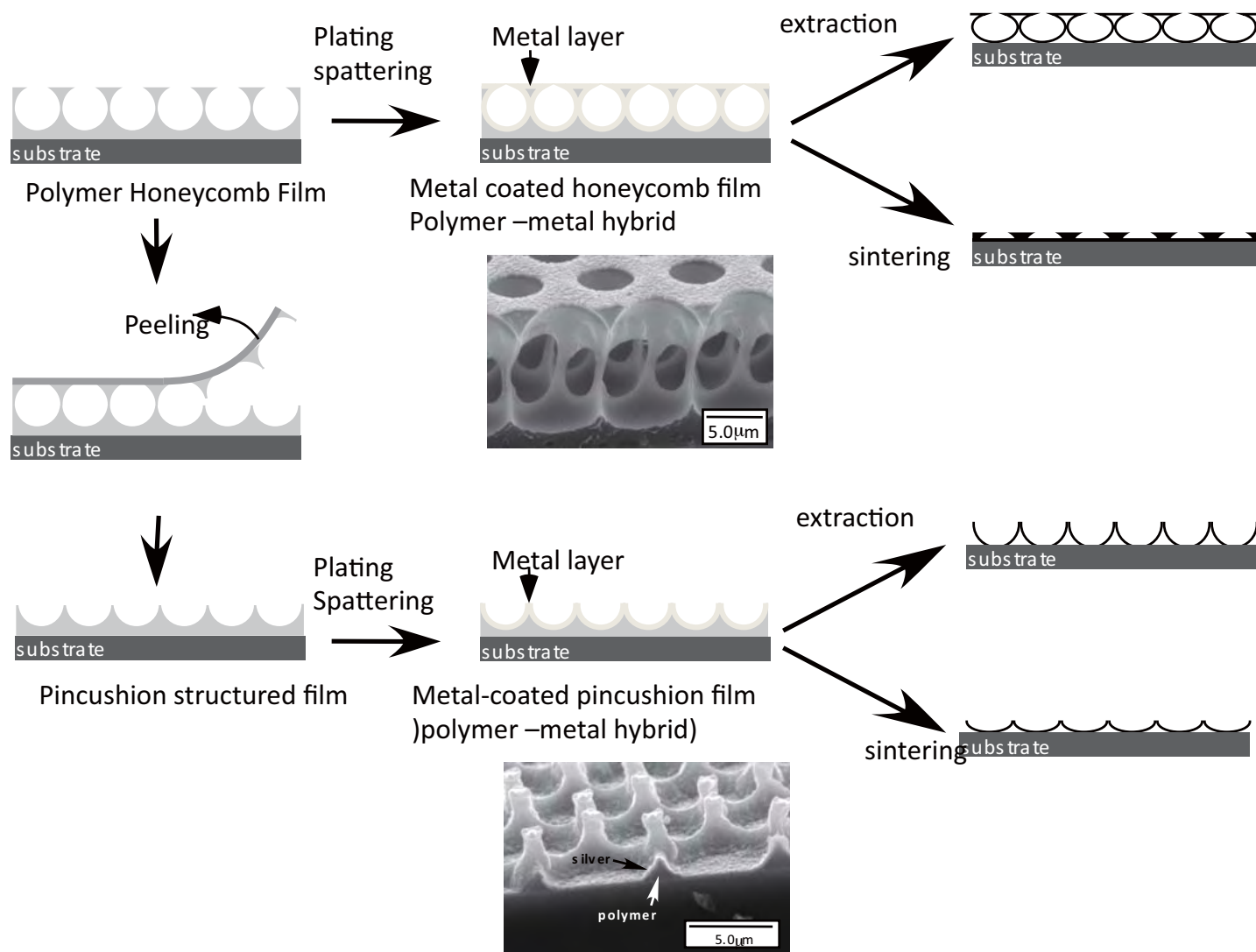
Simple Fabrication of Micro Lens Arrays

Hiroshi Yabu^{*,†,‡,§} and Masatsugu Shimomura^{†,‡,§}

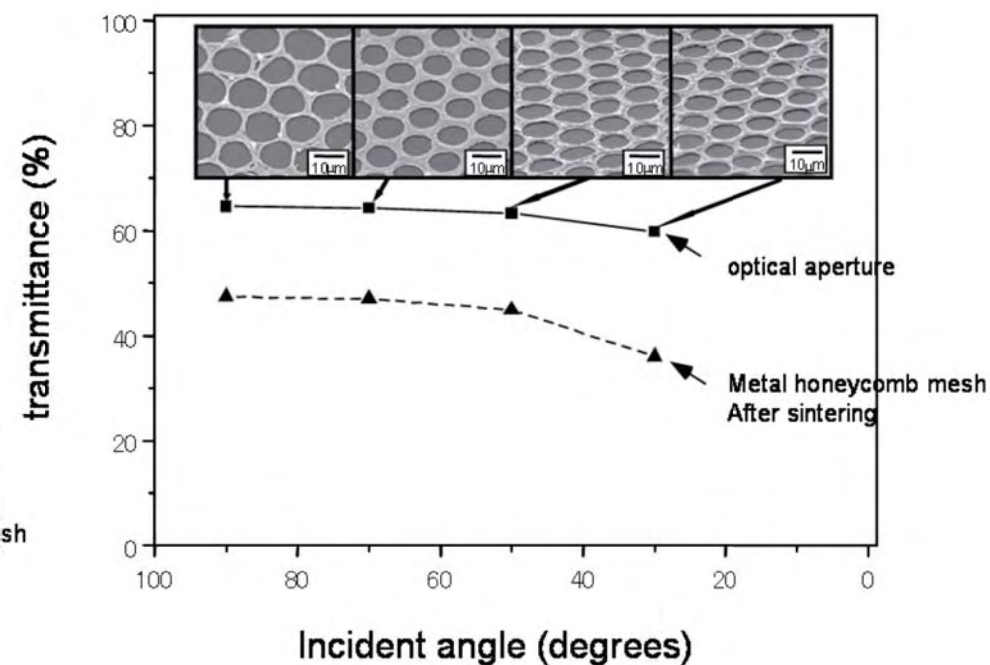
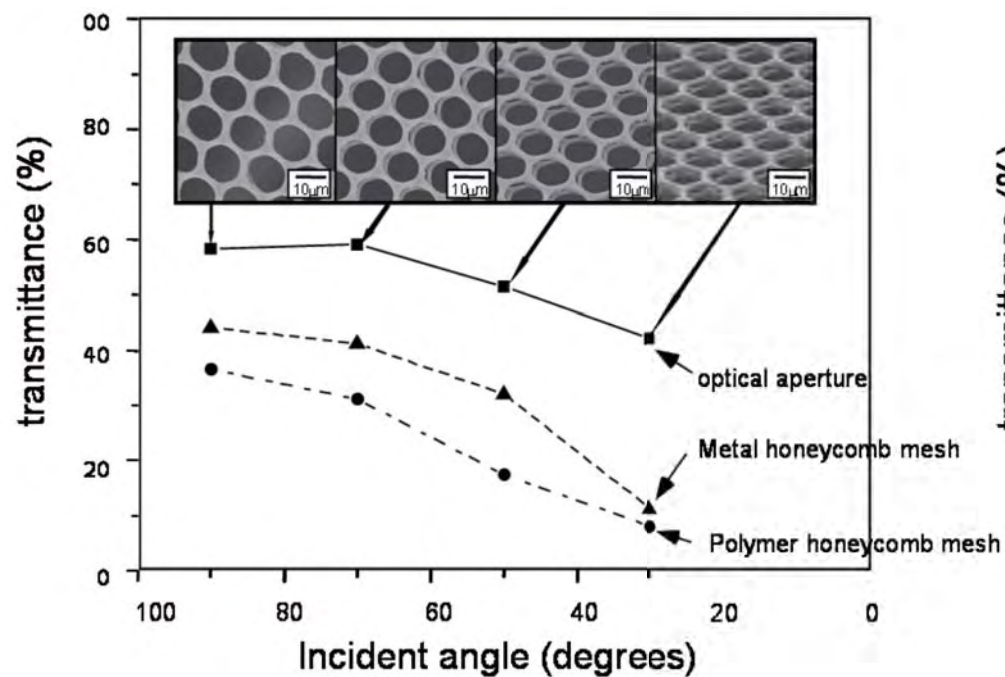
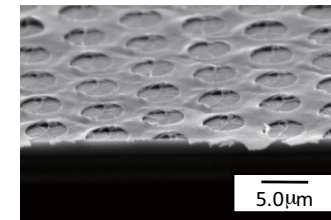
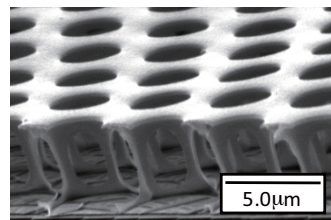


Electroless Plating of Honeycomb and Pincushion Polymer Films Prepared by Self-Organization

Hiroshi Yabu,^{*,†,§} Yuji Hirai,^{||} and Masatsugu Shimomura^{*,†,§}



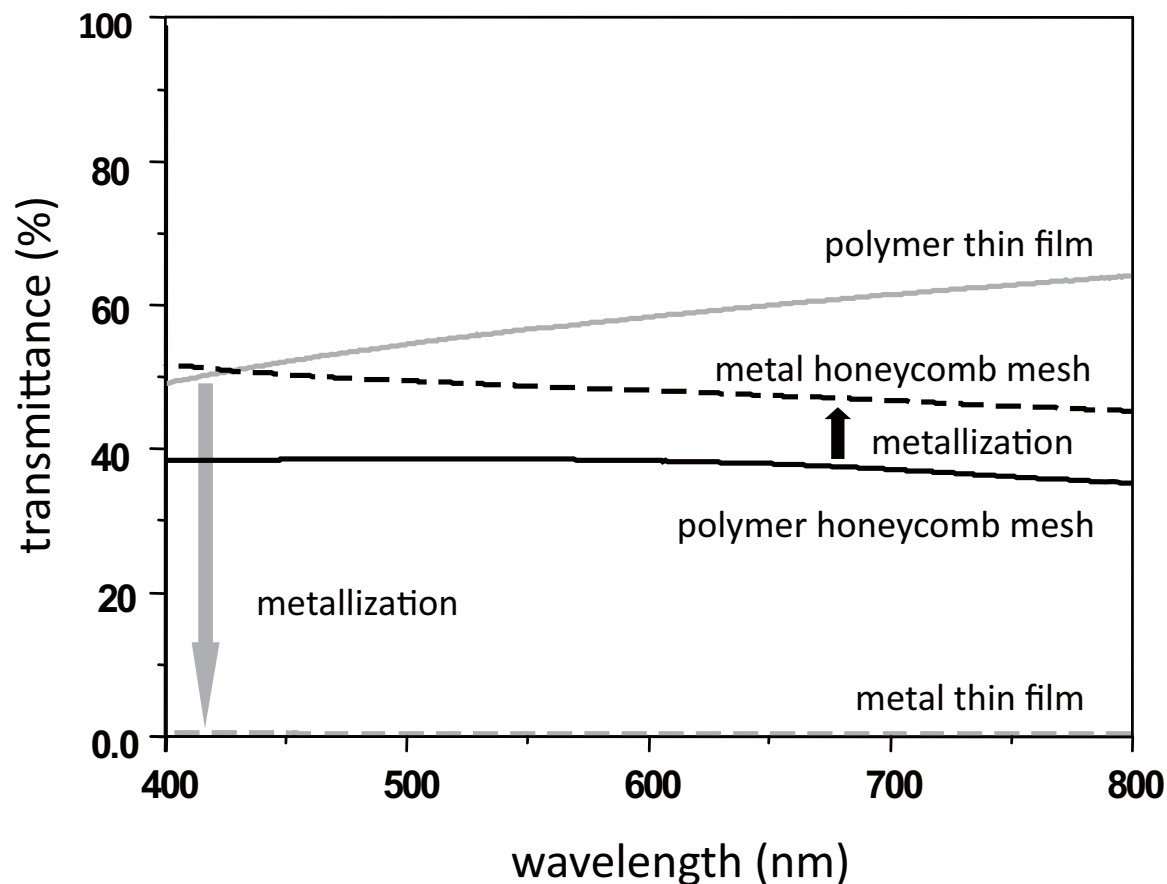
Optical Properties of Metalized Honeycomb Films





Double-Layered Metal Mesh Film With Limited Viewing Angle Prepared by Electroless Plating of Self-Organized Honeycomb Film

Hiroshi Yabu,^{*1,2,3} Yuji Hirai,⁴ Yasutaka Matsuo,⁵ Kuniharu Ijio,⁵
Masatsugu Shimomura^{1,2,3}



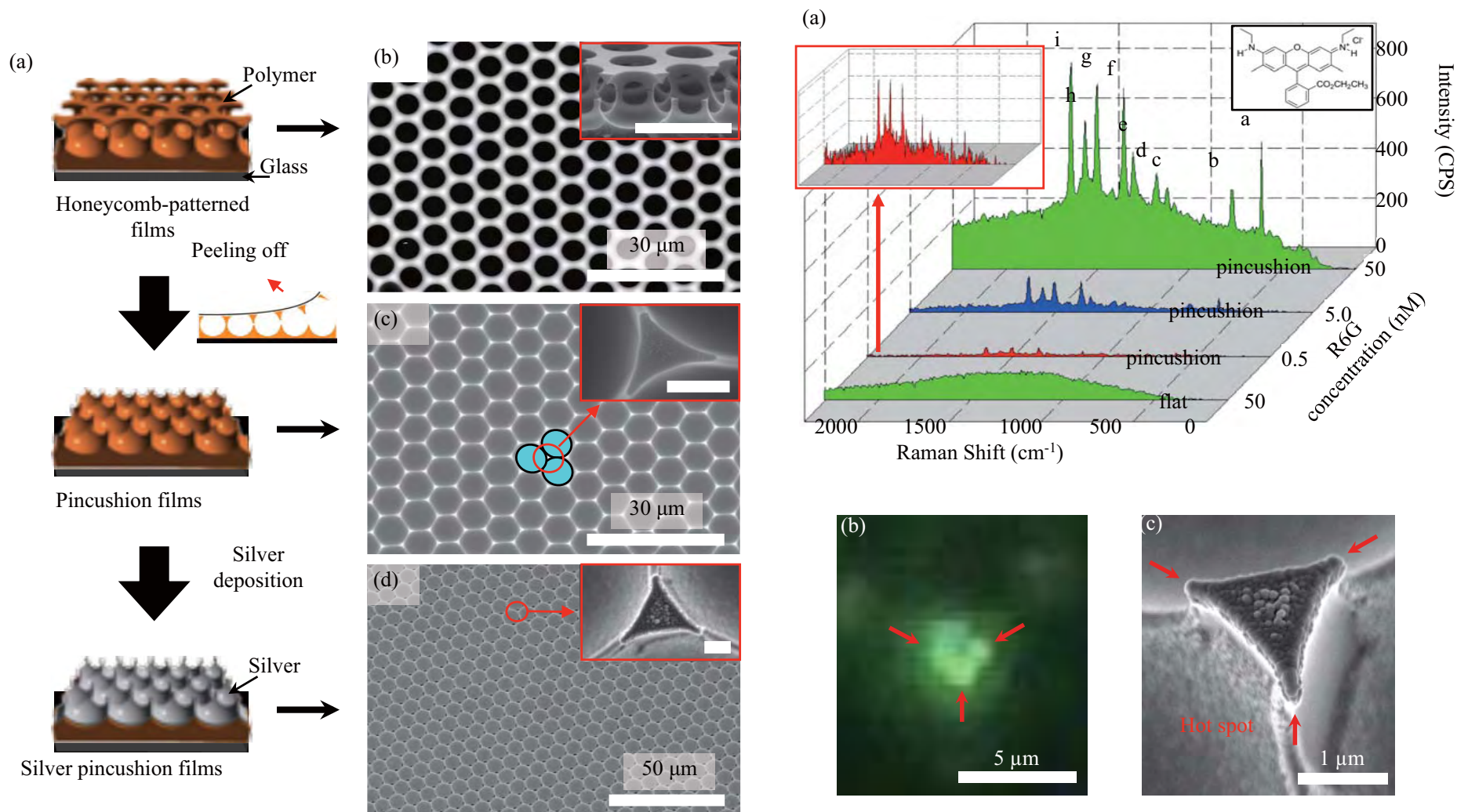
metal honeycomb mesh



polymer honeycomb mesh

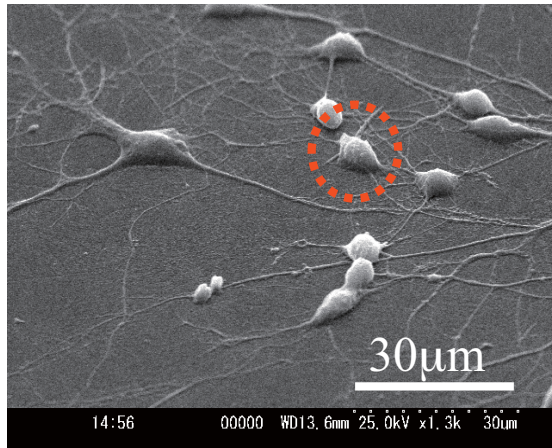
Silver Pincushion Arrays Prepared by Self-Organization and Vapor Deposition Enhance Raman Scattering

Yuji Hirai, Hiroshi Yabu, Yasutaka Matsuo, Kuniharu Ijiro, and Masatsugu Shimomura

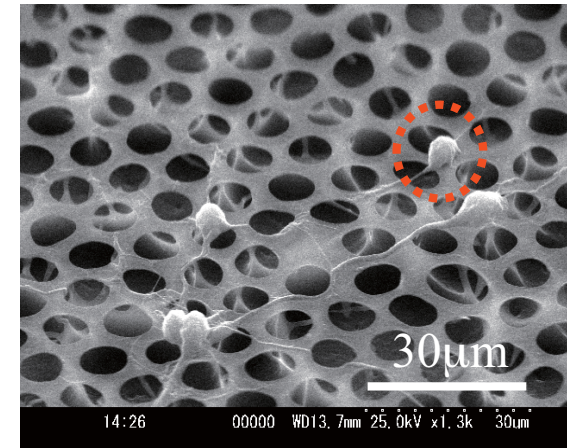
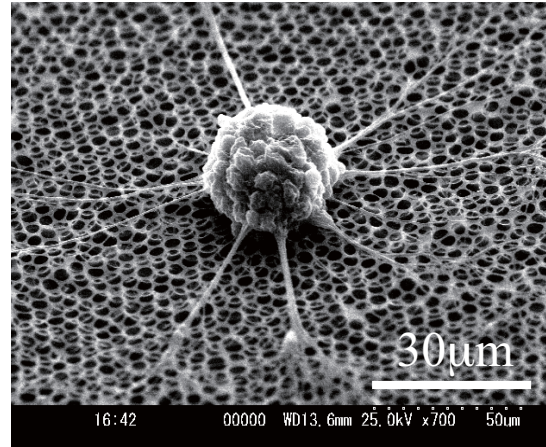


Pore-size Effect on Cultured Hippocampus Neural Cells on Honeycomb Patterned Films

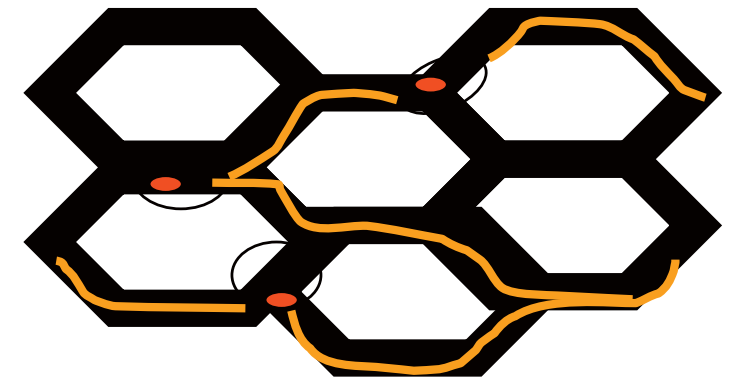
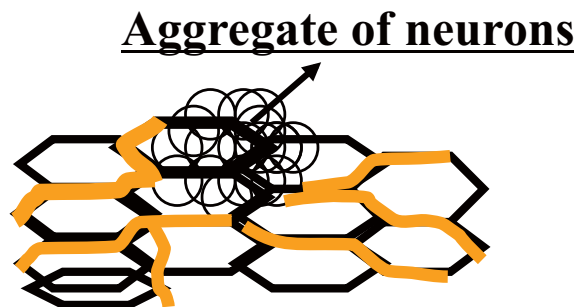
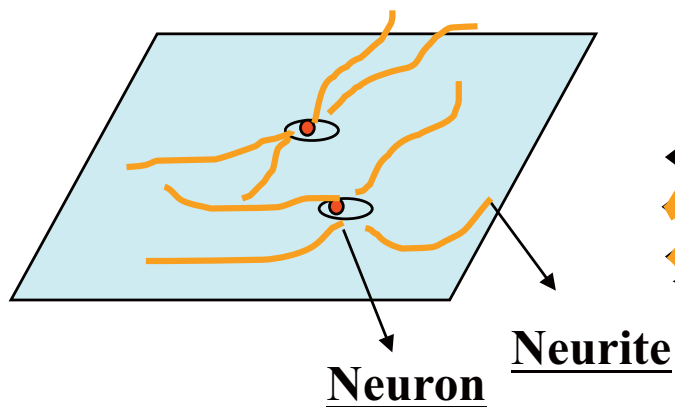
Proliferation of Stem Cells



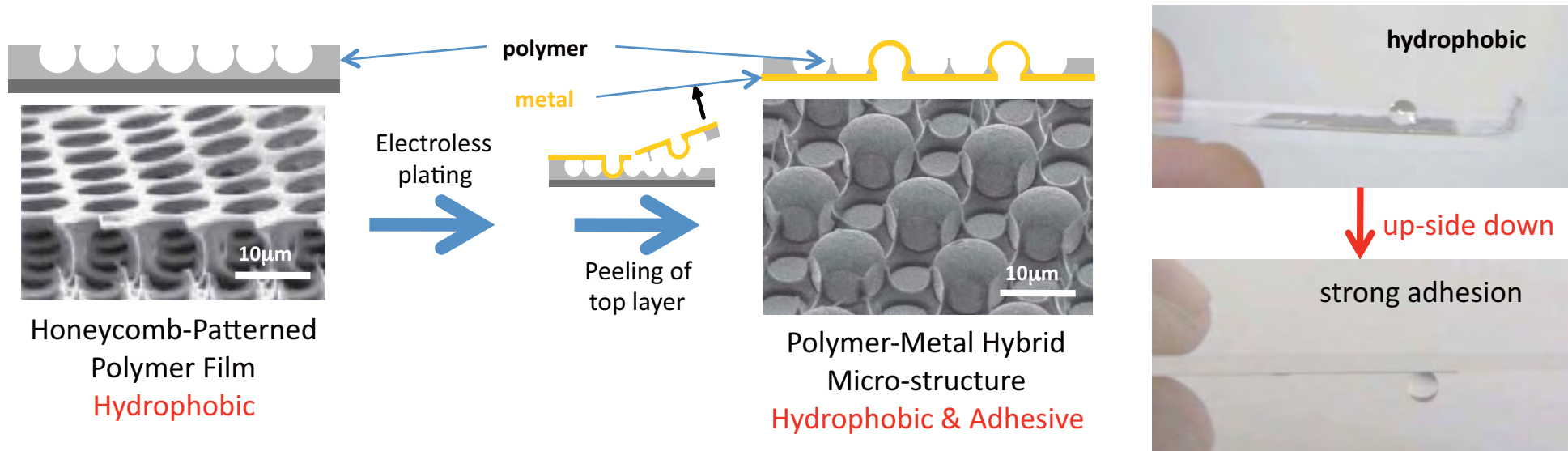
Differentiation to Neuron



Differentiation to Neuron

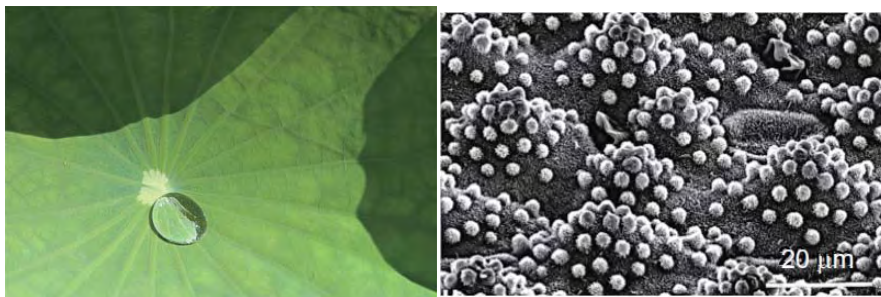


Self-Organized Superhydrophobic Hybrid Nano-& Micro-Materials with Controllable Adhesive Force



Chem.Mater., 21, 1799 (2009)

Background: Biomimetic Approach of Engineering Self-organized Polymer Materials



Neinhuis, C.; Barthlott, W. *Annals Bot.* 1997, 79, 667.

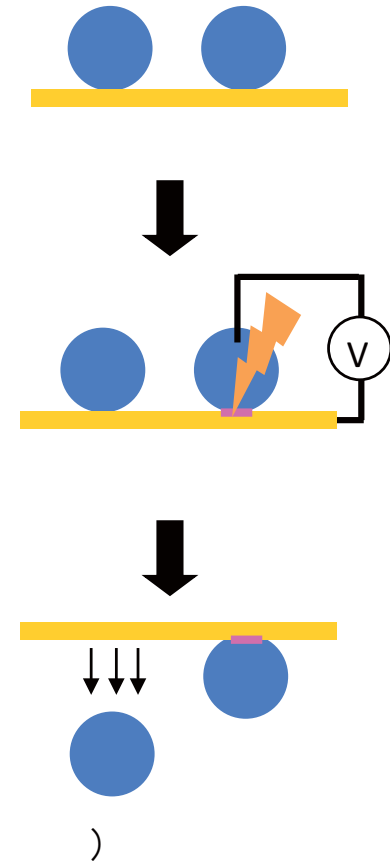
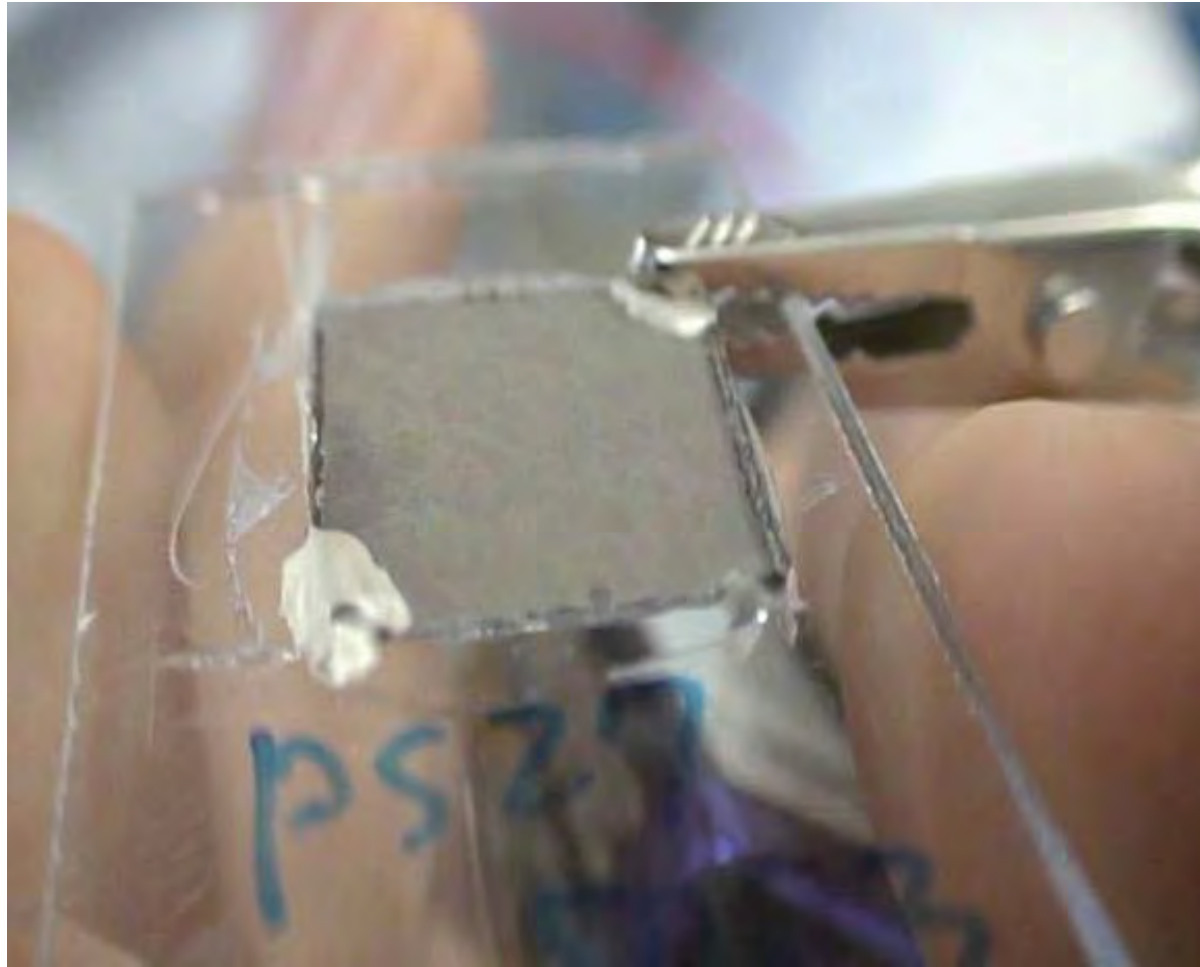
Lotus leaf effect : Hydrophobic surface



Lin Feng, Lei Jiang, et.al. *Langmuir* 2008, 24, 4114

Rose petal effect:
Hydrophobic surface with High Adhesion

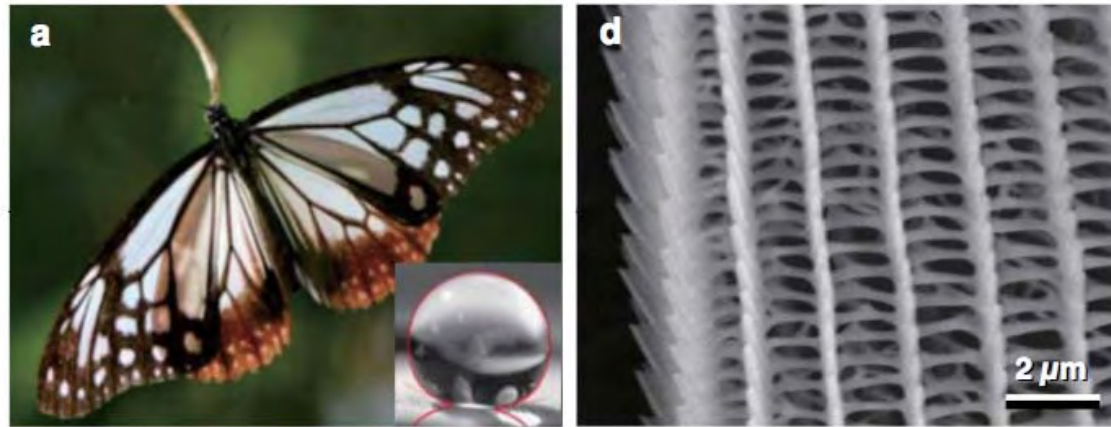
Water droplet manipulation by electric stimuli



From Biomimetic to Bioinspired

Multi Functional Properties Based on Hierarchically Structured Biological Surfaces.

- Toward Biomimetic Material Design -



P.Perez Goodwyn, Naturwissenschaften (2009)

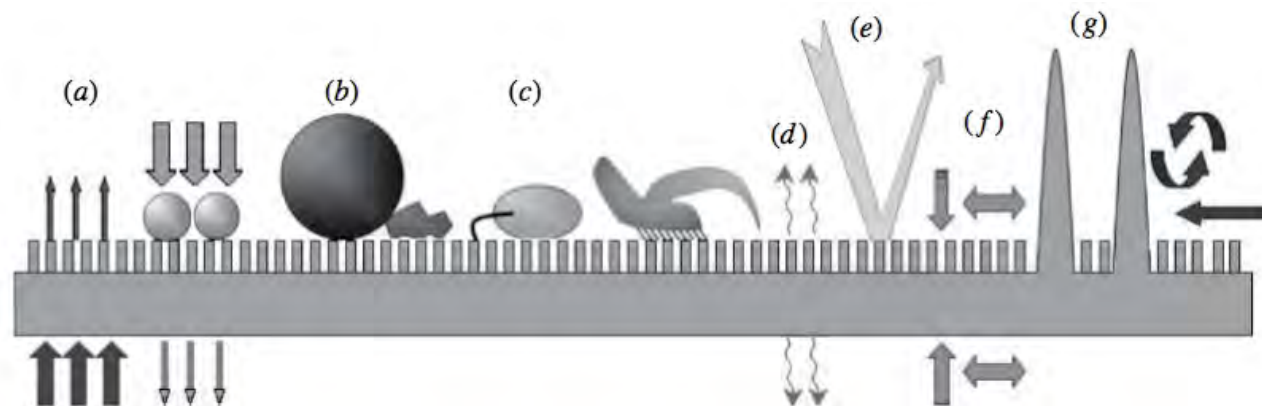


Figure 3. Schematic of the most prominent functions of the boundary layer on a hydrophobic microstructured plant surface. (a) Transport barrier limitation of uncontrolled water loss/leaching from interior and foliar uptake, (b) surface wettability, (c) anti-adhesive, self-cleaning properties: reduction of contamination, pathogen attack and reduction of attachment/locomotion of insects, (d) signalling: cues for host-pathogens/insect recognition and epidermal cell development, (e) optical properties: protection against harmful radiation, (f) mechanical properties: resistance against mechanical stress and maintenance of physiological integrity, and (g) reduction of surface temperature by increasing turbulent air flow over the boundary air layer (Koch *et al.* 2009).

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Moth Eyes and Cicada Wings for the Solar Cells and Windows of the Future

Insects and nanotechnology

By **Stefan Anitel**, Science Editor
 24th of October 2007, 11:30 GMT

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What's the link between insects and solar cells? Bugs hold the secret - improved photocells.

Peng Jiang, an assistant professor of chemical engineering at the University of Florida, gets his inspiration from the eyes of moths and the wings of cicadas in developing new anti-reflective and water-repellent coatings, with huge potential for new more effective and self-cleaning solar cells, car and home windows, computer screens and other devices. "Nature is an amazing innovator. What I'm interested in doing is mimicking the structure of some remarkable biological systems for real-world use.", said Jiang.

Moth eyes are built up of adjacent hexagonal eyelets, each one filled with thousands of neat rows of tiny bumps (nipple-like protrusions). As each bump is less than 300 nanometers (300 billionths of a meter), only an electron microscope can visualize them.

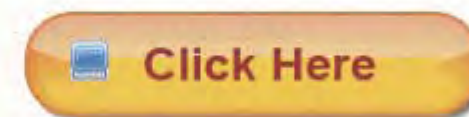
When light hits the eye, the bumps manipulate its reflection to zero, as moths, mostly nocturnal, don't reflect moon or starlight, since by doing so they could betray their position to possible predators. "Engineers have sought to replicate the eyes' microscopic structure using a printing technique called lithography, but it is expensive and ill-suited to creating the extremely tiny rows of protrusions that make the moth eyes so effective." said Jiang.

Jiang appealed to spin coating, which does not try to carve out the pattern on a surface, but constructs the pattern up from building blocks.

Jiang added a liquid suspension of nanoparticles on a circular silicon wafer, similar to that employed in photovoltaic cells. The wafer spanned the suspension, so that the centrifugal force distributed the liquid equally. By drying the liquid, an ordered particle pattern was left behind. This relatively low-tech technique delivered a moth eye-like anti-reflective coating for glass and plastic layer. Jiang even managed to use the technique to silicon wafer surfaces by applying a specific cicada wing trait. "Cicada wings are amazingly effective at rapidly shedding water and dirt, apparently because the insects often need to fly in humid environments," said Jiang.

The wings resemble the structure of the moth eyes, but it is orientated in such a way not to deflect the light, but to expel water droplets, using tiny air pockets surrounding each bump. When the researchers placed a drop of water on a stamp-sized wafer coated with the novel material, the drop moved over the surface till it got to its edge. "The anti-reflective coating may improve the performance of solar cells because it would increase the amount of light the cells receive," said Jiang.

Current solar cells reflect over 10 % of the light, while with the new coating, this could plummet to under 2 %. "The water-repelling element would be useful for keeping the cells clean - a necessity because dirt or dust easily dulls their performance. Rain or simply hosing the coated cells down would clean them adequately. The coatings could also improve the performance of ordinary windows on cars or homes, increasing visibility and reducing the need for cleaning. Numerous challenges remain, including learning how to "scale up" the spin coating process so that it could be used for industrial production", he said.



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Honeycomb-like architecture produced by living bacteria, *Gluconacetobacter xylinus*

Yasumitsu Uraki ^{a,*}, Junji Nemoto ^a, Hiroyuki Otsuka ^a, Yutaka Tamai ^a,
Junji Sugiyama ^b, Takao Kishimoto ^a, Makoto Ubukata ^a, Hiroshi Yabu ^{c,d,e},
Masaru Tanaka ^{c,f,g}, Masatsugu Shimomura ^{c,d,e}

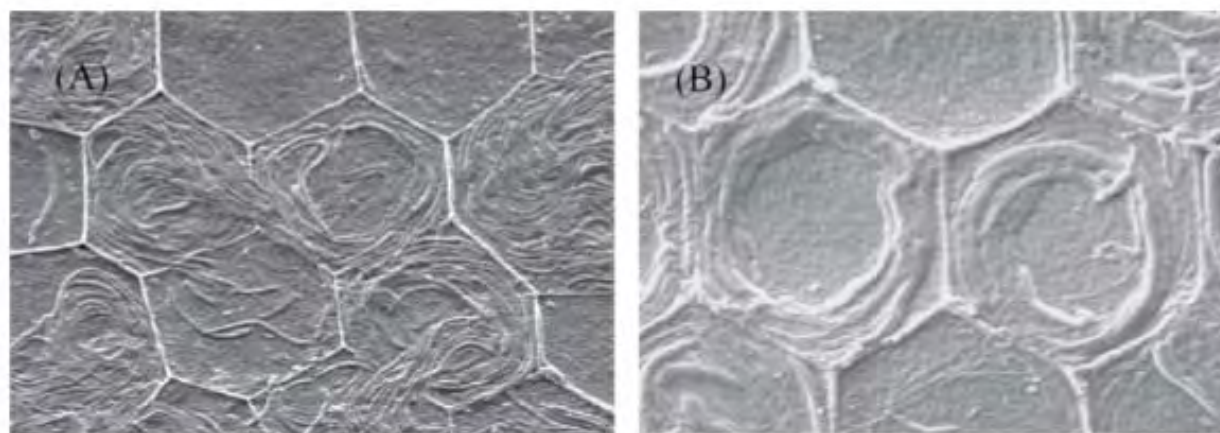


Fig. 2. *Gluconacetobacter xylinus* cultured on (A), cellulose and (B), agarose convex type honeycomb-patterned films placed on flat agarose gels.

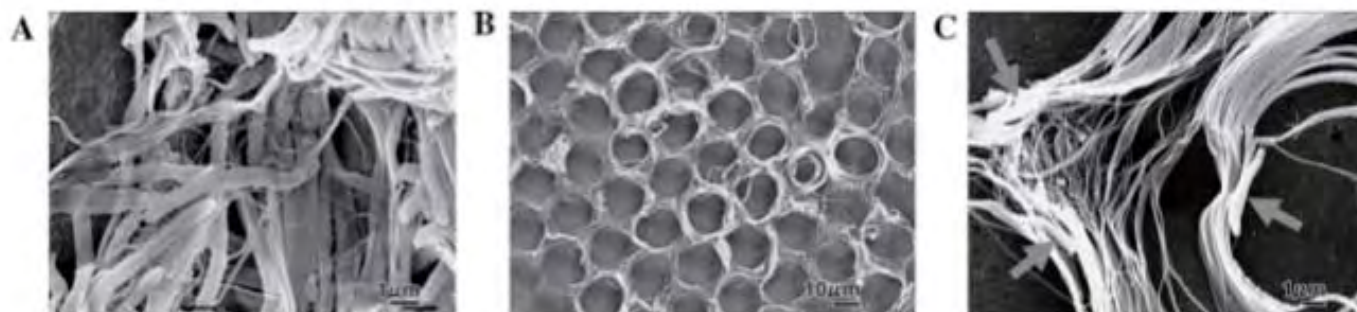


Fig. 5. *Gluconacetobacter xylinus* cultured on honeycomb-patterned agarose under humid conditions in (A) air and (B) humid CO₂ atmosphere. (C) shows a magnified image of (B). Arrows indicate bacteria.