

FleXARs - Everything-free surface

Large-area <u>Flex</u>ible Polymers with <u>Antifouling Robust</u> Micro-<u>s</u>tructure for Marine and Medical Applications

Presented by

Dr. Nithi Atthi (Research Team Leader)

Surface and Microfluidic Device Innovation Research Team (SMDRT)
Thai Microelectronics Center (TMEC)



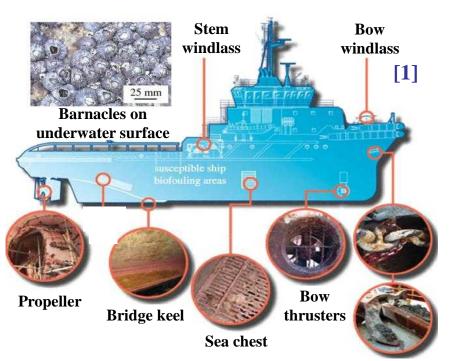


Biofouling



Marine field

(Barnacle attachment on ship)

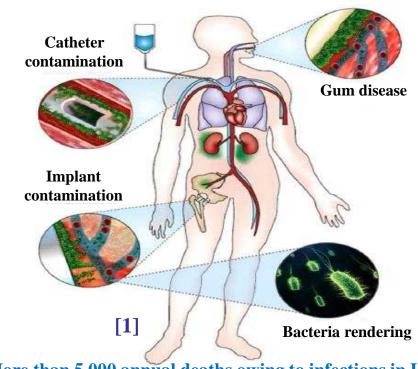


Overall cost for hull repair is 150B USD-/ year Anchor locker

Biofouling in marine environment

- Ship hull drag, fuel consumption
- CO₂ emission, invasive species
- Corrosion, High maintenance cost

Medical field (Body susceptible to infectious biofilms)



More than 5,000 annual deaths owing to infections in US.

Biofouling in surgical/medical site

- Bacterial infections
- Catheter and implant contamination
- Health risks and financial losses

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Biofouling on ship hull and pier **TMEC**Thai Microelectronics Center







Biocidal paint (TBT, Cu)





TBT: Tributyl Tin paint

Cu: Copper-based paint

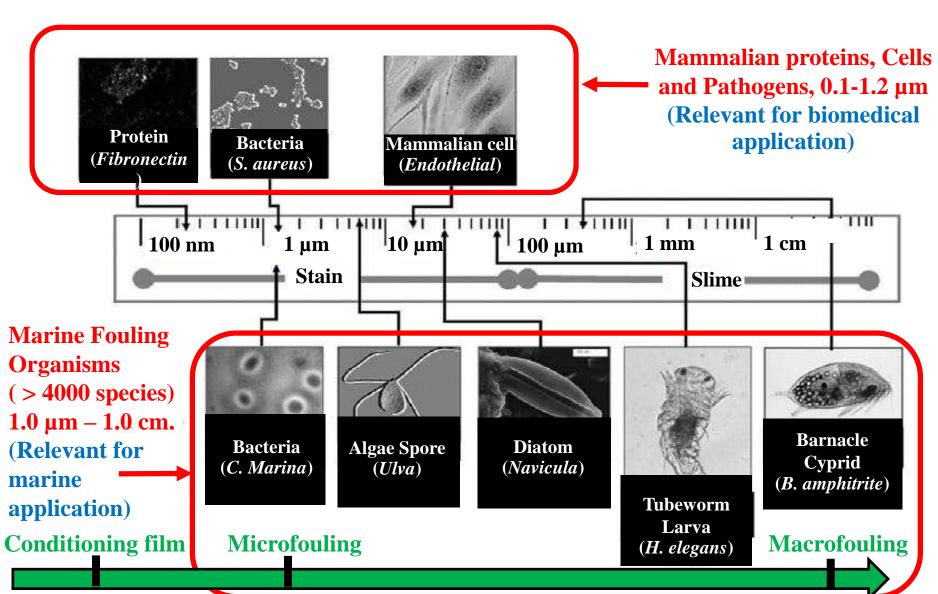
Inflection in surgery room



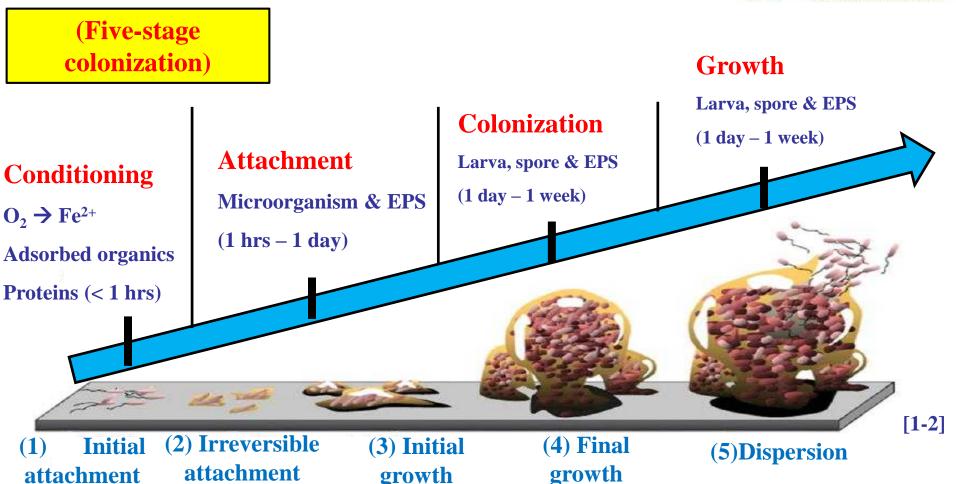


Hierarchy of fouling organisms





Fouling mechanism (Biofilm formation) EC



- Surface wettability influences fouler colonization
- Superhydrophobic is required to prevent an initial attachment

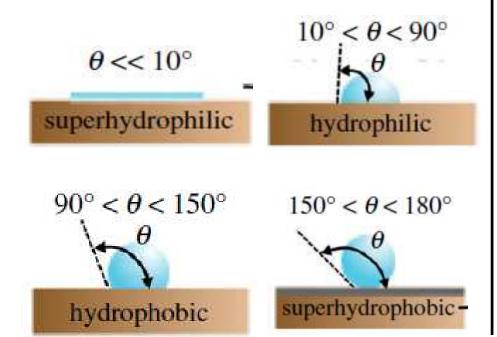
[1] G. D. Bixler and B. Bhushan, *Phil. Trans. R. Soc. A*, 370, pp. 2381-2417 (2018).

[2] J. A. Callow and M. E. Callow, *Nature Communications*, 2, pp. 1-10 (2011).

Antifouling mechanism



Superhydrophobic surface (Water repellent surface)

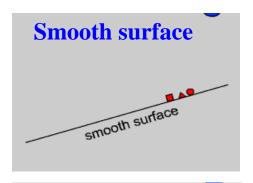


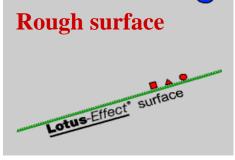
Superhydrophobic surface

Low surface energy Rough surface materials (γ_s)



(Micro-patterns)



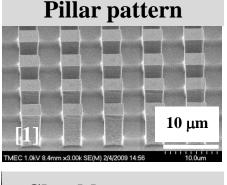


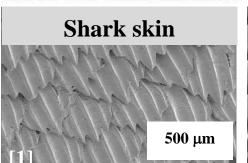
- Superhydrophobic ($\theta > 150^{\circ}$).
- Lotus effects that makes a self-cleaning mechanism
- **Antifouling surface**

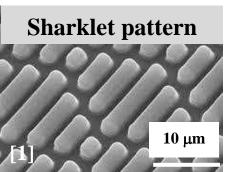
Biomimetic superhydrophobic surface EC

Biomimetic micro-patterns

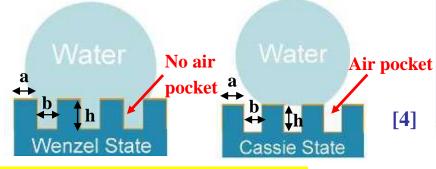
Lotus leaf [3] 10 μm







Effects of surface roughness



Wenzel regime (no air pocket)
$$cos\theta = R_f cos\theta_f; R_f = \frac{A_{SL}}{A_F}$$
 (1)

Cassie-Baxter regime (air pocket)

$$cos\theta = R_f f_{SL} cos\theta_f - 1 + f_{SL}$$
 (2)

 R_f : roughness factor

 $\theta_{\mathbf{f}}$: contact angle on solid surface

 θ : WCA, fSL: fractional solid – liquid contact area

To obtain antifouling surface (superhydrophobicity; $\theta > 150^{\circ}$)

- Low γ_s material (Polydimethylsiloxane, PDMS $\rightarrow \gamma_s$: 12.3 mJ/m²)
- Highest $R_f \rightarrow$ Max. packing factor (P = a/b) + Max. aspect ratio (A.R. = h/a)

a: pattern size, b: space between pattern, h: pattern height, P: Packing factor, A.R.: Aspect ratio

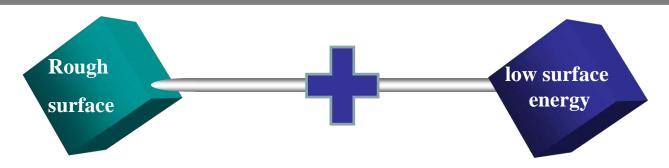
[1] G. D. Bixler and B. Bhushan, *Phil. Trans. R. Soc. A*, 370, pp. 2381-2417 (2018).

[3] C. Neinhuis and W. Barthlott, Ann. Botany, 79, pp. 667-677 (1997). [4] J. Genzer and K. Efimenko, Biofouling, 22 (5), pp. 339-360 (2006).

Artifacts hydrophobic surface



Techniques to make Superhydrophobic surfaces



Method to make a rough surface:

- Lithography and etching
- ***** Electrochemical reaction and deposition
- **❖** Mechanical abrasion
- ***** Crystallization control

Low surface energy materials:

- > Fluorocarbons: Teflon, PFOS, etc.
- > Silicones: TPFS, PDMS, SFS
- Organic materials: PE, PS, polyamide, etc.
- Inorganic materials: ZnO, TiO₂

TPFS: trichloro(1H,1H, 2H,2H-perfluorooctyl)silane

PDMS: Polydimethylsiloxane SFS: Semiflourinate silane

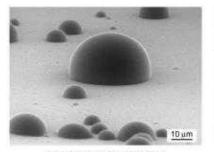
ESEM images of water droplet on pattern That Microelectronics Center



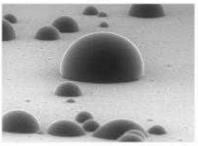
Contact angles on flat and patterned surfaces in an ESEM Increasing condensation

Increasing evaporation

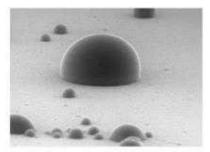
Flat



Static contact angle (98°)

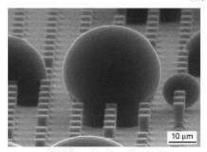


Advancing contact angle (101°)

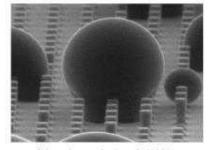


Receding contact angle (95°)

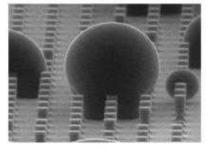
5-µm diameter, 10-µm height, and 12.5-µm pitch pillars



Static contact angle (129°)

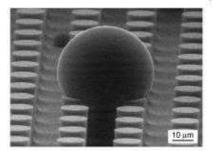


Advancing contact angle (132°)

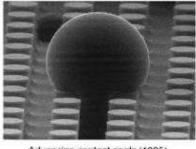


Receding contact angle (127°)

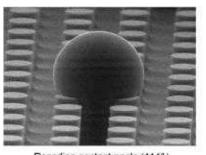
14-μm diameter, 30-μm height, and 26-μm pitch pillars



Static contact angle (126°)



Advancing contact angle (130°)



Receding contact angle (114°)



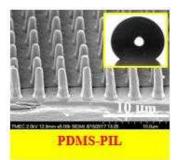
Fouling rel Antifouli Technolog	ing	Antifouling (Marine app.)	Anti Bacterial (Medical app.)	Environ mental/ hospital friendly	Trans parency	Large-area application	Cost
Water jet cleaning https://www.kamat.de/en					*		\$\$ \$ 33/m²/5 years
Biocide paint (TBT, Cu) www.imo.org/en				*	*		\$\$ \$ 67/m²
Ultrasonic wave http://www.ultrasonic- antifouling.com	((((ULTRASONIC))))		*	*	*		\$\$\$\$ \$ 267/m ²
SLIPS® https://wyss.harvard.edu	Slippery Liquid Infused Porous Surface	*					\$\$\$ >\$ 200/m ²
Sharklet® https://www.sharklet.com		*					\$\$\$ > \$ 200/m ²
FleXARs							\$ \$ 20/m ²

Milestone of FleXARs project

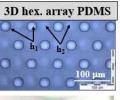


- Superhydrophobic surface on silicon and glass substrate
- Ultra-hydrophobic surface
- Ultra-oleophobic surface
- Si mold fabrication
- Soft lithography process of PDMS

PTT project Phase#1 (Micro-patterns for barnacle antifouling)



Antibacterial/ algae antifouling field test







Composite PDMS/PU

Superoleophobic surface

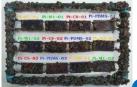
Pattern size scaling

Large-area patterning (R2R NIL production)

Field-test in marine and medical applications

2008-2014

2015



PDMS: Polydimethylsiloxane

PU: Polyurethane

2016

2017

PTT project phase#2 (micro-scale patterned on PDMS and PU)

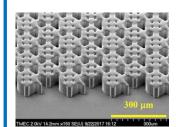
Black resin as 2nd mold for various resin casting

Field-test in seawater environment

3D microstructure

2018

Robust micro-structure



2019-2022

2023-2024

Spin-off

(Commercialization)



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Nanoparticles (NPs) Vs FleXARs // TMEC

Properties	Nanoparticles (NPs)			FleXARs	
Materials	Ag	TiO ₂	Ag+TiO ₂	ZnO	Composite PDMS-PU
Objectives/ applications	Antibacterial applications	for <u>Medic</u>	al, Food, and	<u>Textile</u>	Antifouling for BOTH marine and medical applications
Core Technology	Ag, Zn: Adhere to cell wall → lead to cell death Ti: Photocatalytic redox effect (Need UV, light)			Robust microstructure on low surface energy materials	
Fabrication method	Milling, Laser ablation, Etching, Pyrolysis, Sol-gel, Precipitation, Thermal decomposition, Green synthesis, Vapor deposition			Soft lithography (+Stitching casting) ** R2R NIL	
Action	Active action (Biocide, Bacteria killer)			Passive action (Reduce protein adsorption)	
Mechanism	(1) Oxidative stress induction(2) Metal ion release(3) Non-oxidative mechanisms			Superhydrophobic/Oleophobic with low surface energy materials	
Advantages/ Differentiate	Low-cost and large-area applications Applicable to various surfaces			Robust pattern, durable in seawater, biocompatible	
Disadvantages	Difficult to control the Dimension and size of NP Too many toxic and hazardous by-products Biocide and non-environmental friendly		Small sample size (10x10 cm) Low throughput Degrade with high temperature		

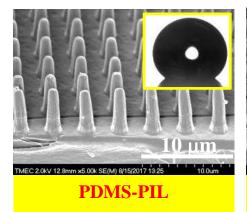
FLEXPOL VS FleXARs

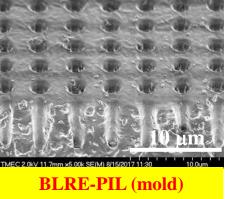


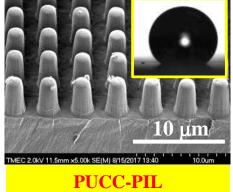
		That Microelectronics	
Properties	FLEXPOL [1]	FleXARs	
Materials	Polypropylene (PP)	Composite PDMS-PUA	
Objectives	Antimicrobial adhesive film	Non-biocide antifouling film	
Applications	Medical applications	Marine and medical applications	
Core Technology	(SLIPS) Essential oil emulsions embedded in PP micro- patterns matrix	 (Superhydrophobic +oleophobic) Robust microstructure Low surface energy materials 	
Fabrication	Roll-to-roll Nano-imprint lithography (R2R-NIL) +R2R process for large-area patterning with low-cost manufacturing		
Robustness	Very weak	Very robust	
Swelling in seawater	Yes	No	
Biocompatible (Non-biocide)	Yes		

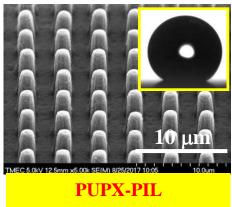
Micro-patterning of Polymers

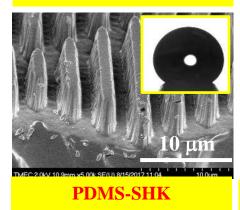


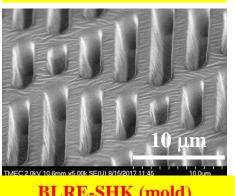


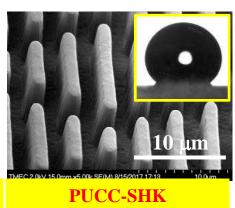


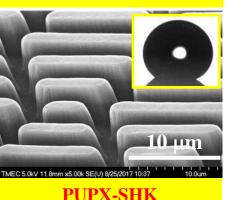












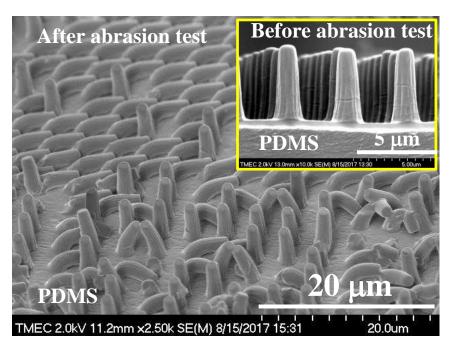
BLRE-SHK (mold)

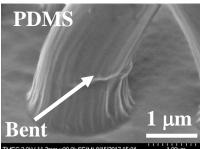
PUPX-SHK

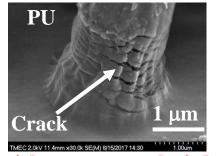
	Mold castability/Pattern qualities			WCA [degree]		
Materials				using 3 µL of water droplet		
Materials	Mold	Air	Pattern collapse	Flat	Pillar	Sharklet
	releasable	bubbles	after mold release	(FLT)	(PIL)	(SHK)
PDMS (Sylgard-184)	Yes	No	No	117±1.3	143±1.4	146±2.7
PU (Crystal clear 204)	Yes	No	No	100±4.6	152±5.7	148±4.2
PU (PX5210)	Yes	No	No	104±3.3	145±1.7	148±7.4

Issue: Pattern collapse

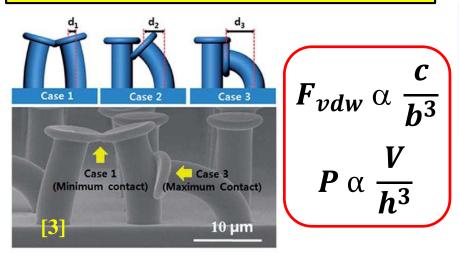








Pattern mating & clumping



h: pillar height, V: displacement of pillar, c: contact area b: distance between pillar

- Soft and flexible (σ: 5.0 MPa, ε: 116%)
- Hardly replicate dense pattern (a < 400 nm) with high A.R. (> unity)
- Pattern mating and clumping $(P < F_{vdw})$

3D microstructure with two-steps height is required to maximize displacement and minimize contact area to prevent pattern mating and pattern clumping ($P > F_{vdw}$)

Note: Mating is pillar-to-pillar interactions (lateral collapse).

Clumping is pillar-to-substrate interactions (ground collapse).

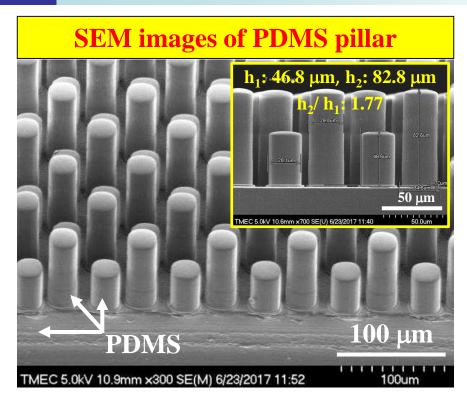
[1] N. Atthi, et. al., J. Nanosci. Nanotechnol., 11, pp. 1-7 (2011).

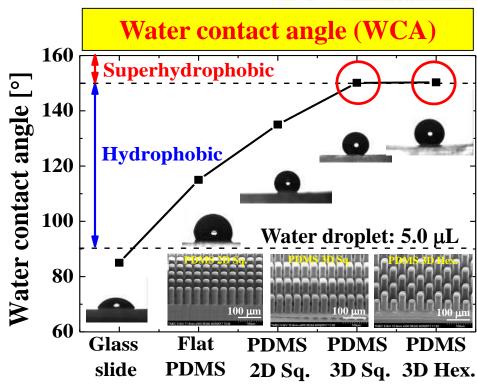
[3] W.-G. Bae, et. al., Soft Matter, 9, pp. 1422-1427 (2013).

Pulling force (P) is a recovery force.

3D Microstructure, WCA and CAH







- Pattern height is under-estimated due to loading effects during Bosch etching process.
- 3D Sq. and 3D Hex. → Superhydrophobicity.
- Lower CAH → Low adhesive contaminant and self-cleaning surface.

Pillar type	WCA [°]	CAH [°]
2D Sq.	139.2±4.0	6.2
3D Sq.	150.1±2.9	2.9
3D Hex.	150.3±4.2	1.2

3D microstructure increases surface roughness and decreases pattern displacement

Bacterial antifouling performance

Bacteria adhesion assay

E.coli adhesion on PDMS samples

UV sterilization (Prevent pattern collapsed)

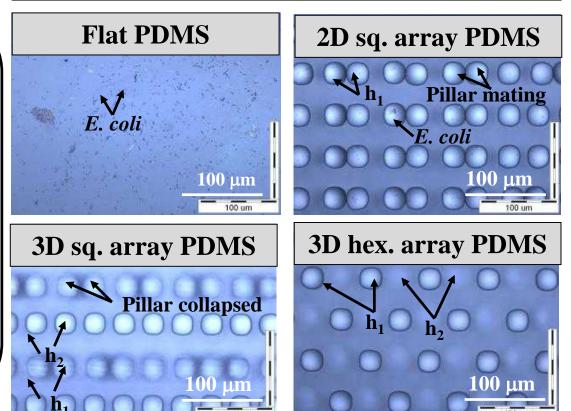
Immersed in Nutrient broth with inoculated E. coli. ATCC 8739

 $(\sim 10^5 \text{ CFU/mL})$ at 37°C/7 days

Rinse with PBS

Dyed with Gram's stain

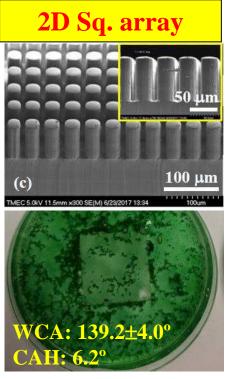
OM measurement

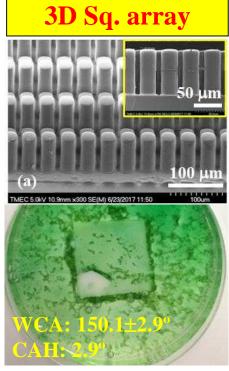


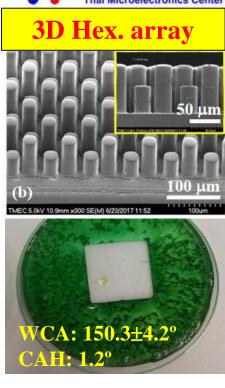
- UV sterilization is not degrade the PDMS pattern qualities compared to other sterilization methods (Autoclave, Ethanol, Ethylene).
- 3D Hex. arrays prevent E. coli adhesion \rightarrow No pattern mating and clumping.

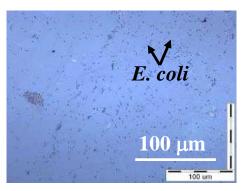
Algae antifouling and Antibacterial TMEC

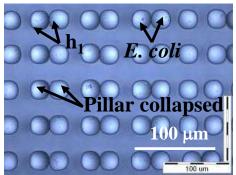


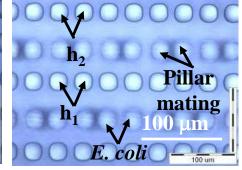


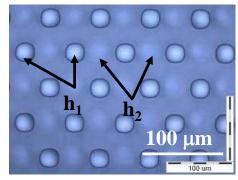












Summary



Large-area Flexible Polymers with Antifouling Robust Micro-structure for Marine and Medical Applications (FleXARs Project)

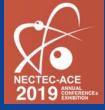
- Environmental-friendly non-biocide antifouling technology
- Low surface energy materials and micro/nano-patterning
- Superhydrophobic and oleophobic surface (Water-and-oil repellent)
- Robust 3-D micro-structures
- Antibacterial and Algae antifouling
- Marine, medical and public transportation applications

TBD: Composite materials + Robust microstructure

+Pattern scaling + Superoleophobic + large-area patterning









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Thai-German Graduate School of Engineering



















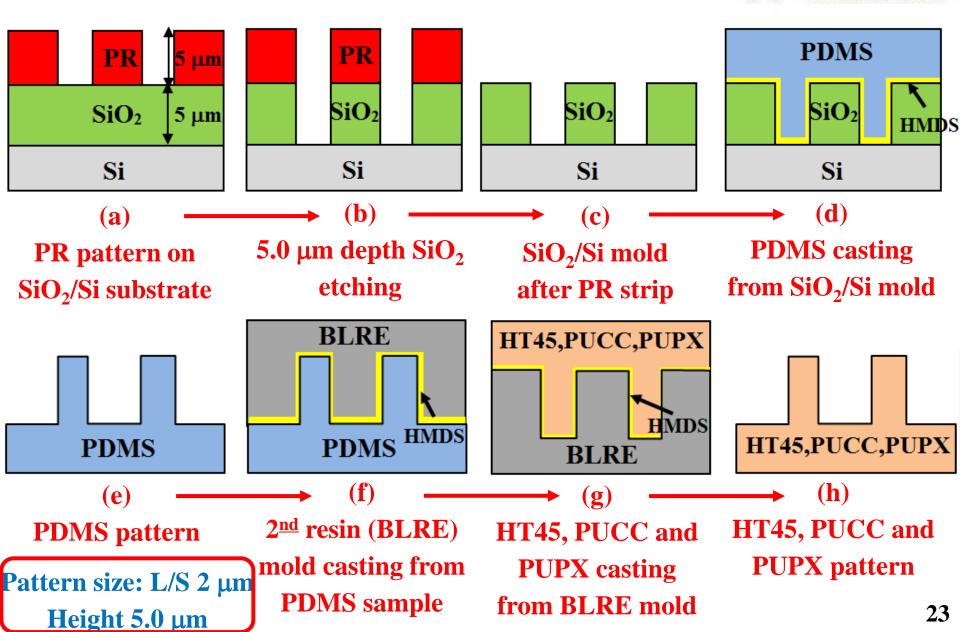




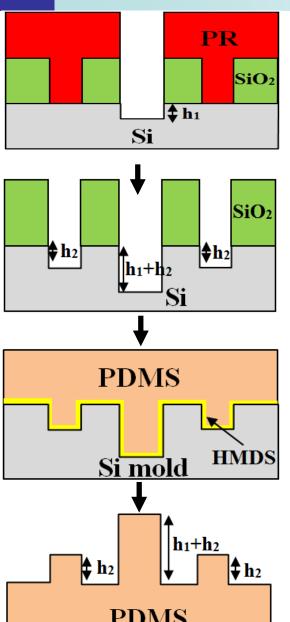


FleXARs: Large-area <u>Flex</u>ible Polymers with <u>Antifouling Robust</u> Micro-structure for Marine and Medical Applications

Soft Lithography (Si mold & 2nd reside That Microelectronics Center



Fabrication of 3D microstructure



PECVD oxide film (5.0 μm)/p-Si(100)

 $1^{\underline{st}}$ lithography (PR: 5.0 μ m, CD: 20 μ m)

Oxide hard mask etching (h, area)

(RIE, CF₄/CHF₃/Ar:10/50/100 sccm, RF:800W/20 min

2nd lithography (CD: 20 μm) + oxide etching (h₁ area)

Si mold

fabrication

(LELE process)

 $1^{\underline{st}}$ Si etching (h₁), (Bosch process: 38 and 75 loops)

Dep.: C₄F₈/SF₆: 200/5 sccm, ICP/RIE: 2000/10W, 8s Etch: SF₆: 400 sccm, ICP/RIE: 200/25W, 5s

PR strip $(O_2 \text{ ashing} + SC1)$

 $2^{\underline{nd}}$ Si etching $(h_1 + h_2)$, (Bosch process: 75 loops)

Dep.: C₄F₈/SF₆: 200/5 sccm, ICP/RIE: 2000/10W, 8s

Etch: SF₆: 400 sccm, ICP/RIE: 200/25W, 5s

PR strip and HMDS priming (48 hrs)
PDMS casting
(Soft lithography)

Curing at 85°C/120 min and release Si mold

SEM, contact angle, contact angle hysteresis (CAH), bacteria adhesion, salt spray corrosive test





FleXARs - Everything-free surface

Large-area Flexible Polymers with Antifouling Robust Micro-structure for Marine and Medical Applications (Pattern design and Conceptual structure)

Presented by

Dr. Nithi Atthi (Research Team Leader)

Surface and Microfluidic Device Innovation Research Team (SMDRT)

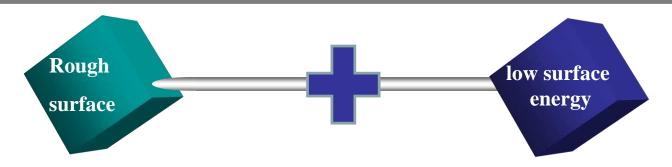
Thai Microelectronics Center (TMEC)



Artifacts hydrophobic surface



Techniques to make Superhydrophobic surfaces



Method to make a rough surface:

- Lithography and etching
- ***** Electrochemical reaction and deposition
- **❖** Mechanical abrasion
- ***** Crystallization control

Low surface energy materials:

- **Fluorocarbons:** Teflon, PFOS, etc.
- Silicones: TPFS, PDMS, SFS
- Organic materials: PE, PS, polyamide, etc.
- Inorganic materials: ZnO, TiO₂

TPFS: trichloro(1H,1H, 2H,2H-perfluorooctyl)silane

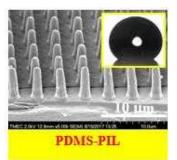
PDMS: Polydimethylsiloxane SFS: Semiflourinate silane

Milestone of FleXARs project

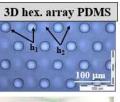


- **Superhydrophobic** surface on silicon and glass substrate
- **Ultra-hydrophobic** surface
- **Ultra-oleophobic** surface
- Si mold fabrication
- Soft lithography process of PDMS

PTT project Phase#1 (Micro-patterns for barnacle antifouling)



Antibacterial/ algae antifouling field test







Composite PDMS/PU

Superoleophobic surface

Robust Pattern and pattern size scaling

Large-area patterning (R2R NIL production)

Field-test in marine and medical applications

2008-2014

2015



PDMS: Polydimethylsiloxane

PU: Polyurethane

2016

2017

PTT project phase#2 (micro-scale patterned on PDMS and PU)

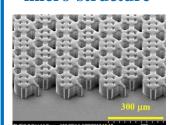
Black resin as 2nd mold for various resin casting

Field-test in seawater environment

3D microstructure

2018

Robust micro-structure



2019-2022

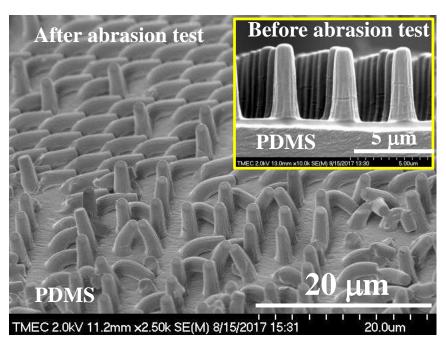
2023-2024

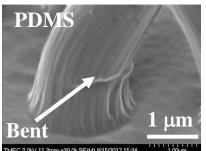
Spin-off

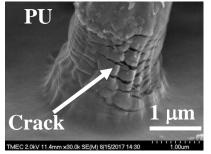
(Commercialization)



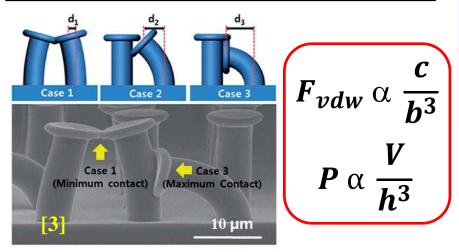
Pattern collapsed by external forces TMEC







Pattern mating & clumping



h: pillar height, V: displacement of pillar, c: contact area b: distance between pillar

- Soft and flexible (σ: 5.0 MPa, ε: 116%)
- Hardly replicate dense pattern (a < 400 nm) with high A.R. (> unity)
- Pattern mating and clumping $(P < F_{vdw})$

3D microstructure with two-steps height is required to maximize displacement and minimize contact area to prevent pattern mating and pattern clumping ($P > F_{vdw}$)

Note: Mating is pillar-to-pillar interactions (lateral collapse).

Clumping is pillar-to-substrate interactions (ground collapse).

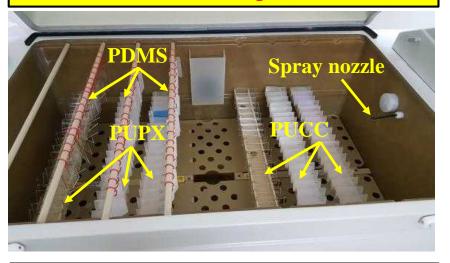
[1] N. Atthi, et. al., J. Nanosci. Nanotechnol., 11, pp. 1-7 (2011).

[3] W.-G. Bae, et. al., Soft Matter, 9, pp. 1422-1427 (2013).

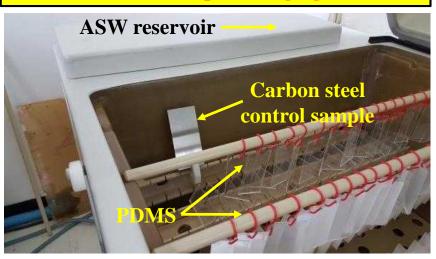
Pulling force (P) is a recovery force.

Salt spray corrosion testing (354 https://www.center.com/

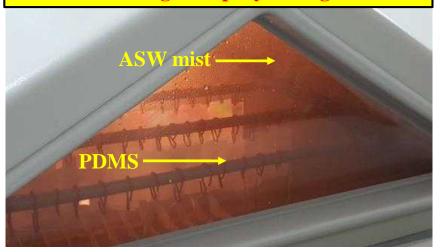
PUCC and PUPX sample (15-30° tilt)



PDMS sample (Hanging)



During salt spray testing



Testing condition(Q-FOG cyclic corrosion tester)

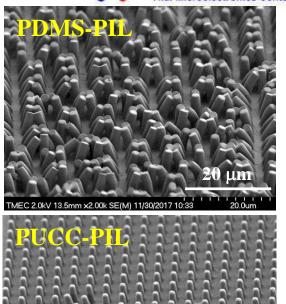
- ASW (ASTM D1141-98)
- pH = 8.314.
- Sample size: 5x10 cm, thickness: 2 mm.
- Sampling: 0, 18, 66, 162, 234, 306, 354 hrs

ASW: Artificial Sea Water

Pillar pattern collapse after SST



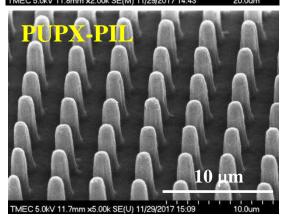
Date	PDMS-PIL	PUCC-PIL	PUPX-PIL
Day 0 (17/10/2017)		<u>100 μm</u>	<u>100 μm</u>
162 hrs (24/10/2017)	100 μm	<u>100 μm</u>	<u>100 μm</u>
354 hrs (01/11/2017)	<u>100 μm</u>	<u>100 μm</u>	<u>100 μm</u>



PDMS: soft and flexible PUPX: Hard and tough

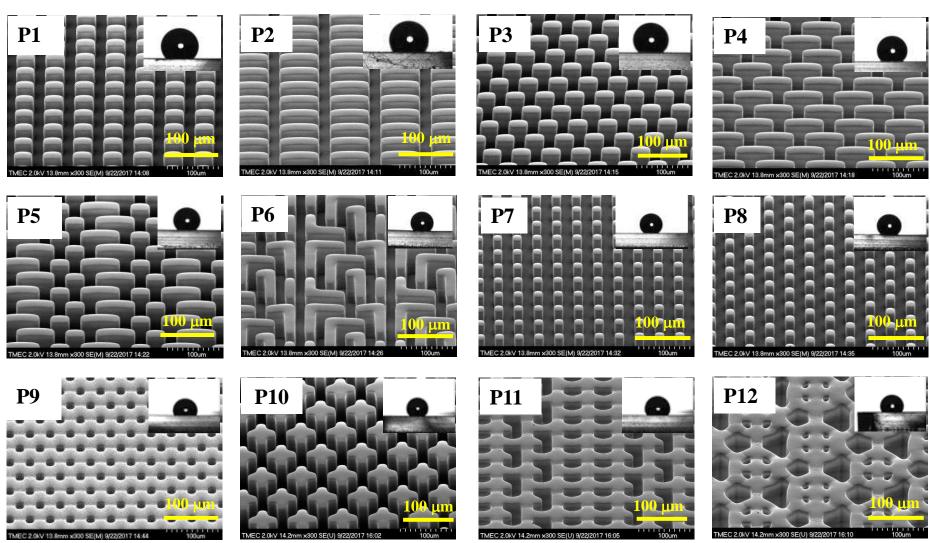
PUCC: Hard and tough

Materials	σ [MPa]	ε [%]	τ [MPa]
PDMS	5	116	1.8
PUCC	53	4.2	34.8
PUPX	16	0.9	41.8



PDMS pattern (Before abrasion) // TMEC

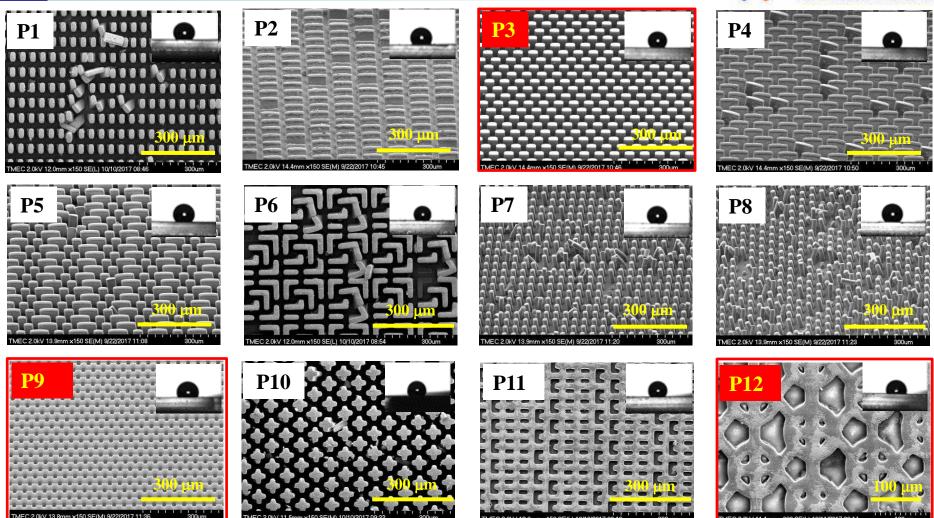




After release PDMS pattern from Si mold, all 12 different PDMS patterns are not collapsed. The pattern sidewall is near vertical. 7

PDMS pattern (After abrasion) // Thai Microelle

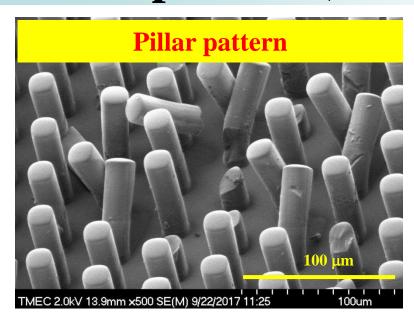


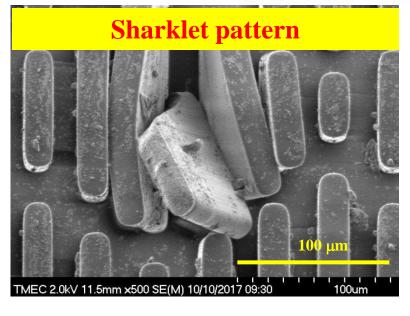


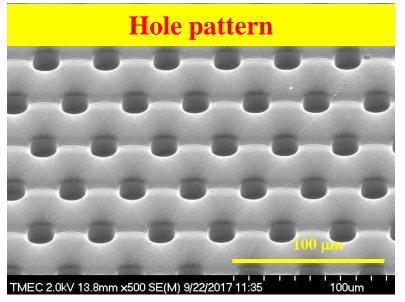
- After abrasion test the samples by hands for 30 cycles, almost PDMS pillar-like patterns (excepted F3) were collapsed.
- Hole-like PDMS patterns (F9, F10, F14) has more durability.

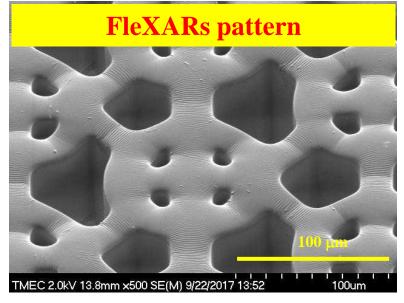
PDMS pattern (After abrasion) TIMEC





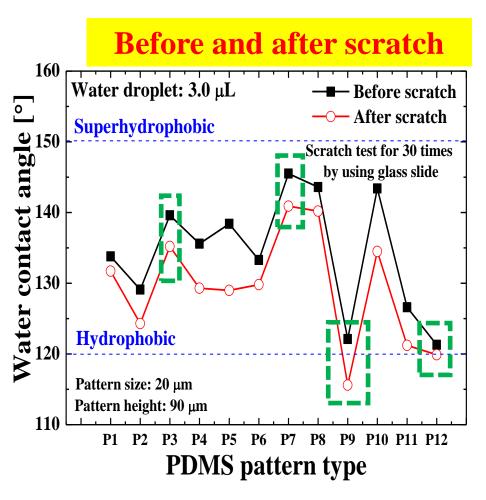


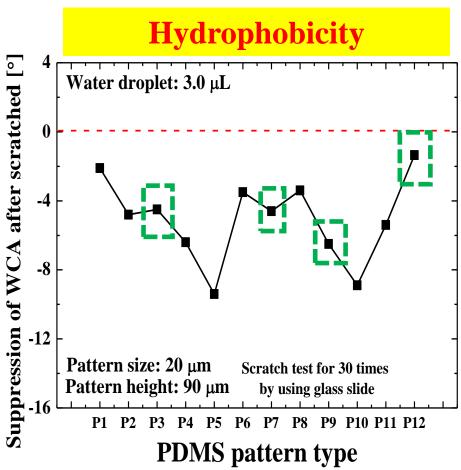




Scratch test Vs Hydrophobicity

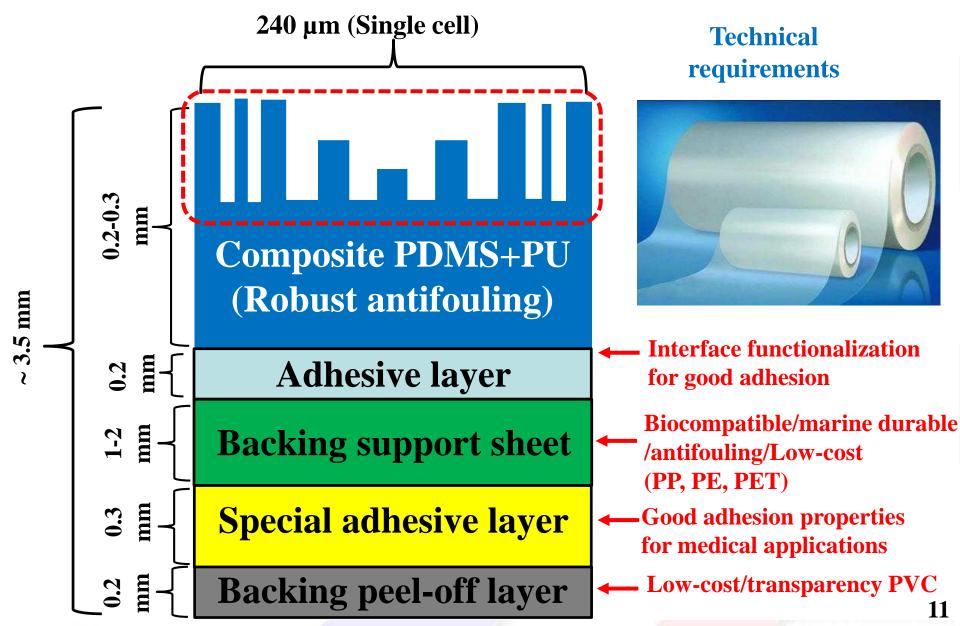






FleXARs film stacks structure

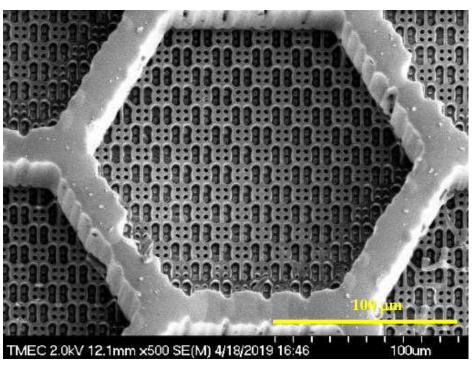


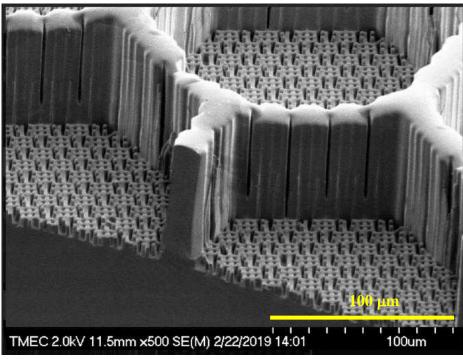




Top-view SEM image





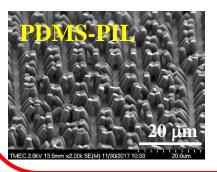


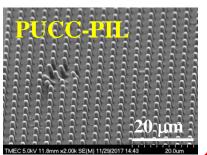
Future plan



(1) Composite PDMS-PU material

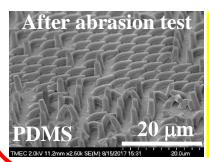
PDMS has swelled and pattern collapsed in seawater while PU has low WCA and not suitable for antifouling in seawater.



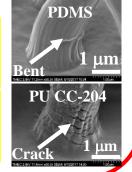


(2) Antifouling robust microstructure with superoleophobic properties

PDMS pattern has collapsed and PU has cracked after abrasion test for 30 cycles. Moreover, WCA has decreased due to oil on seawater surface.

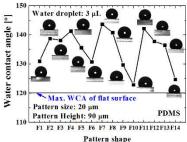


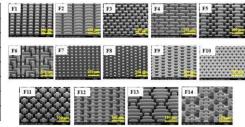




(3) Pattern size smaller than 500 nm

The current pattern sizes are 20 μm and 2 μm , which not small enough to prevent initial attachment stage. Then WCA is lower than 150°





(4) Large-area patterning

The maximum pattern size by using soft lithography from 6 inch Si mold is 10x10 cm. However, largearea sample is required for actual applications.



Target Customers



Health care



Hospital & Veterinary hospital



Nursery, school, living room



Escalator handrails



Trolley in supermarket/airport

Marine applications



Oil-rig platform columns



Container ship, Cruise, Warship



Fiber optic/ telecommunication network

Public transportation



BTS/MRT/ARL systems



Public bus (BMTA)



Train station/bus stop/airport

Summary



Large-area Flexible Polymers with Antifouling Robust Micro-structure for Marine and Medical Applications (FleXARs Project)

- Development of <u>composite biocompatible PDMS-PU materials</u>
- Design robust superoleophobic micro-patterns with guard-ring
- Pattern size scale down below 500 nm
- <u>Large-area patterning</u> by using roll-to-roll process (30 cm width, 100 m length)
- Development a backside <u>glue layer stacks</u>
- Benchmark with SLIPS®, Sharklet®, and FLEXPOL®
- Mass production by R2R NIL
- Target customers/users: PTT, SCG, Hospitals, BTS, MRT, etc.





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FleXARs: Large-area <u>Flex</u>ible Polymers with <u>Antifouling Robust</u> Micro-structure for Marine and Medical Applications