

Surface Engineering Introduction:

Why surface treatment is important?

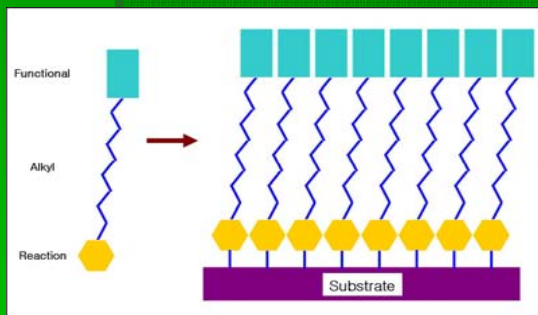
- Soft lithography, microfluidics, thin film coating, semiconductor cleaning process, etc.
- Surface properties: wettability, adhesion, biocompatibility

What kinds of methods can be used?

- Chemical methods
 - SAM: surface modification: hydrophilic vs hydrophobic
 - Piranha solution: surface cleaning (strong acid or base)
- Physical methods
 - Plasma
 - UV or UVO

1. Surface modification by using SAMs

- ◆ Various functionalities
- ◆ Without damage to sensitive device structures



→ Functional group
→ Alkyl chain
→ Reaction group

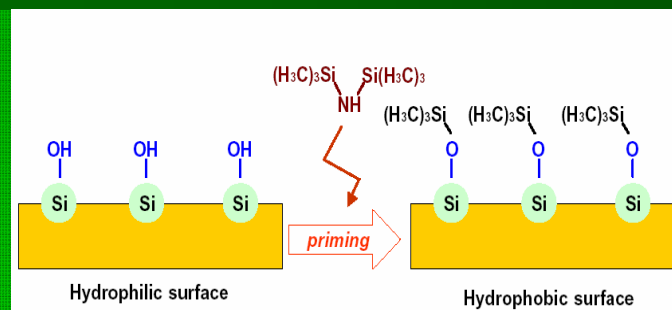
Hydrophobic: $-\text{CH}_3, -\text{CF}_3, -\text{Phenyl}(\text{C}_6\text{H}_5)$
Hydrophilic: $-\text{OH}, -\text{COOH}, -\text{SH}, -\text{NH}_2$

$-\text{SH}, -\text{SiCl}_3, -\text{Si}(\text{OR})_3$



Au, Ag, Pd, Pt

Si, SiO_2 , glass, Cu, Ni, ITO



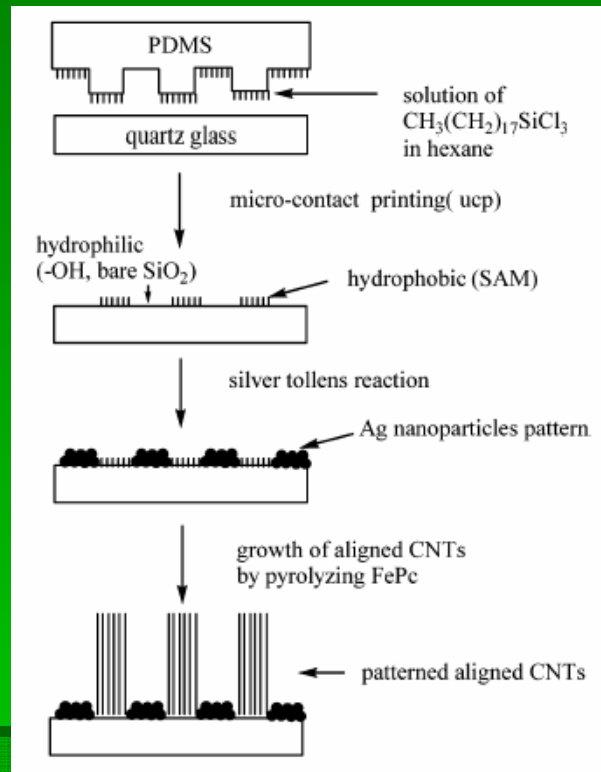
반도체 공정에서 실리콘옥사이드 기판위에 PR의 접착력 증가를 위해서 (HMDS)

Classification of surfaces

nonstick	(+)attracting	(-)attracting	sticky
CH ₃ -	H-terminated Si (Si-H)	NMe ₃ ⁺ terminated SAM	Bare
CF ₃ -	COOH-terminated SAM	C(NH ₂) ₂ ⁺ terminated SAM	Gold
	PO ₃ H ⁻ terminated SAM	NH ₃ ⁺ terminated SAM	
	Oxidized Si (Si-O ⁻)	NMe ₃ H ⁺ terminated SAM	
	Hexaethylene glycol-SAM		

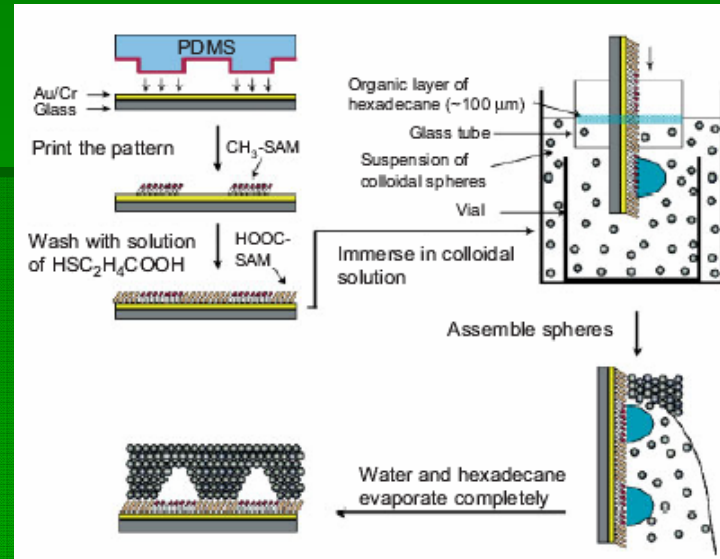
G.M. Whitesides et al, *Langmuir* **1997**, 13, 5355

Selective Growth of CNT



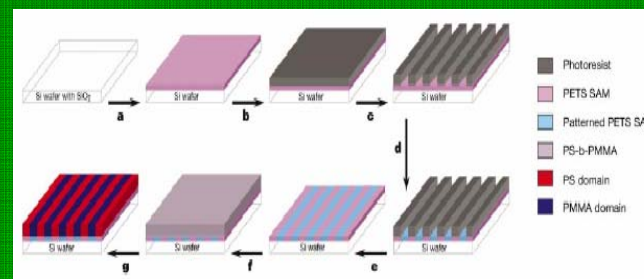
J. Phys. Chem. B, 2003, 3455

Patterned colloidal crystals



Adv. Mater. 2002, 1799

Epitaxial self-assembly pattern of BCs



Nature, 2003, 411

What's problem?

The use of chemicals?

-tricky

If surface reaction groups do not exist?

Convenient & Defect free method?



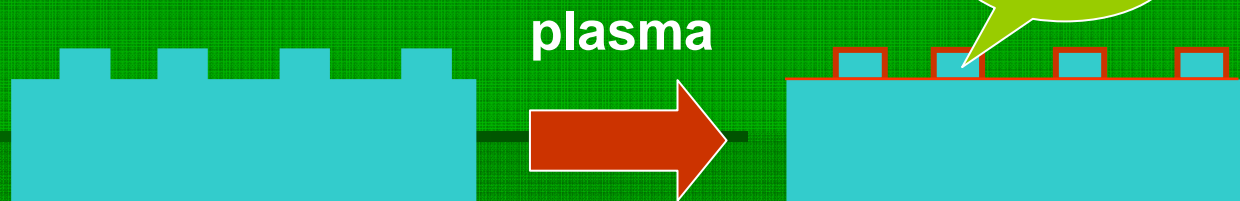
2. Plasma-enhanced surface modification



Plasma cleaner



Reactive ion etcher

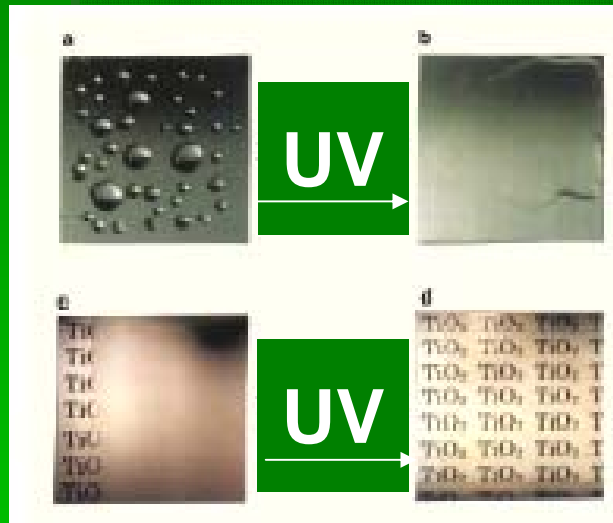


Hydrophobic polymer

Hydrophilic surface

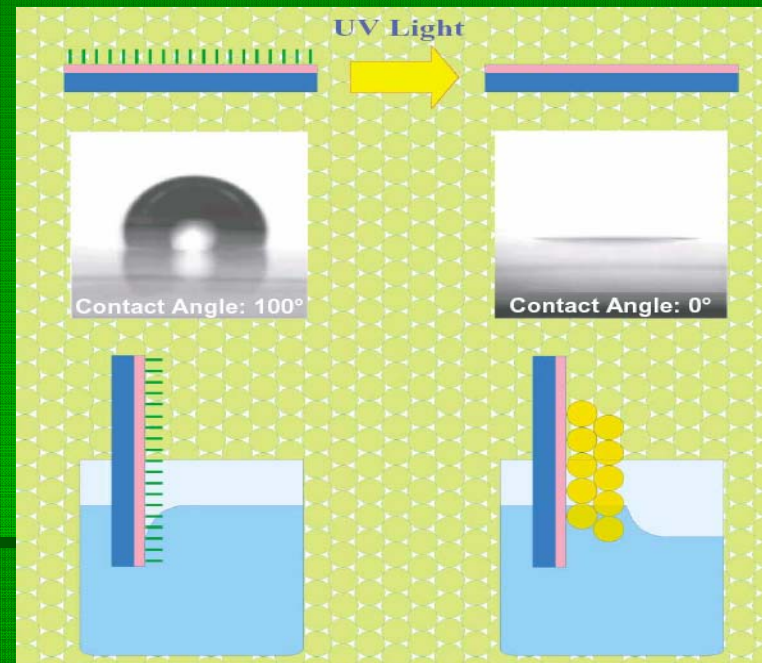
- Sometimes, Plasma (O_2) can cause damage (to the microstructure of polymer surface including PDMS.

3. UV/UVO assisted surface modification

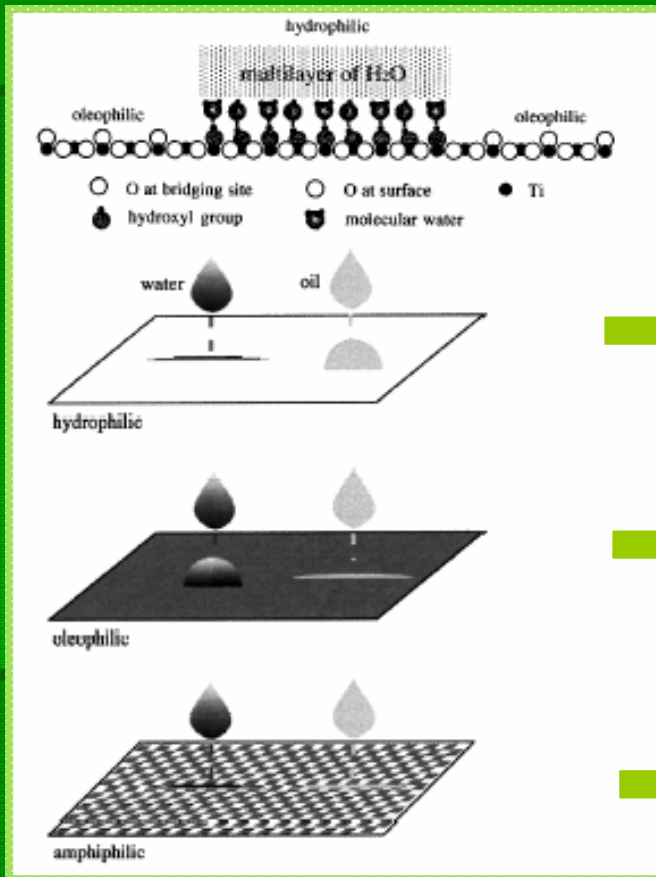


a: Hydrophobic b: hydrophilic
c: fog d: antifogging

Nature, 1998, 431



Angew. Chem. Int. Ed. 2002, 2067



Hydrophilic (After UV irradiation)



Oleophilic



Amphiphilic

A Simple method for the attachment of polymer films on solid substrates



Spin coating
(physisorbtion)



Solvent washing



Easily removed
by rinsing with a
solvent

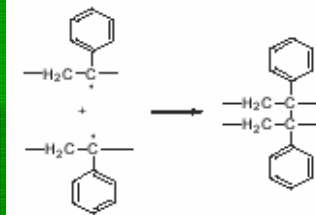


Spin coating & UV
(crosslinking)



Strongly attached
to the surface

Crosslinking



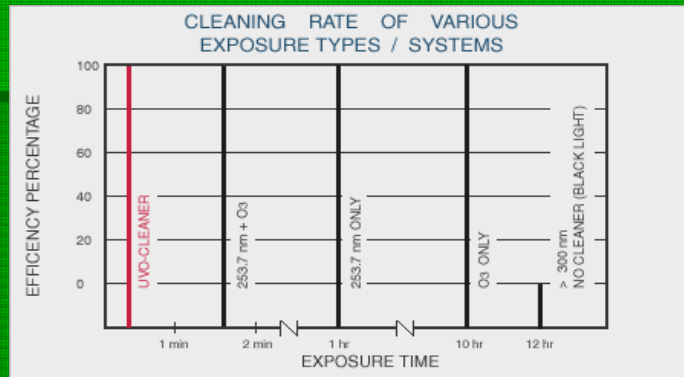
UVO (UV and Ozone)



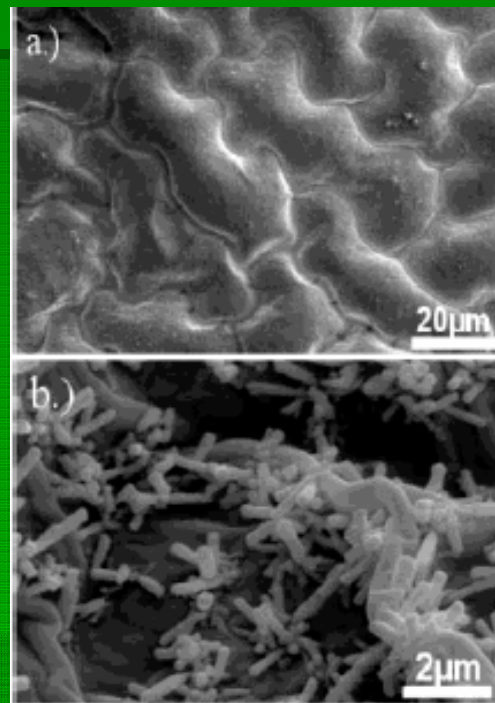
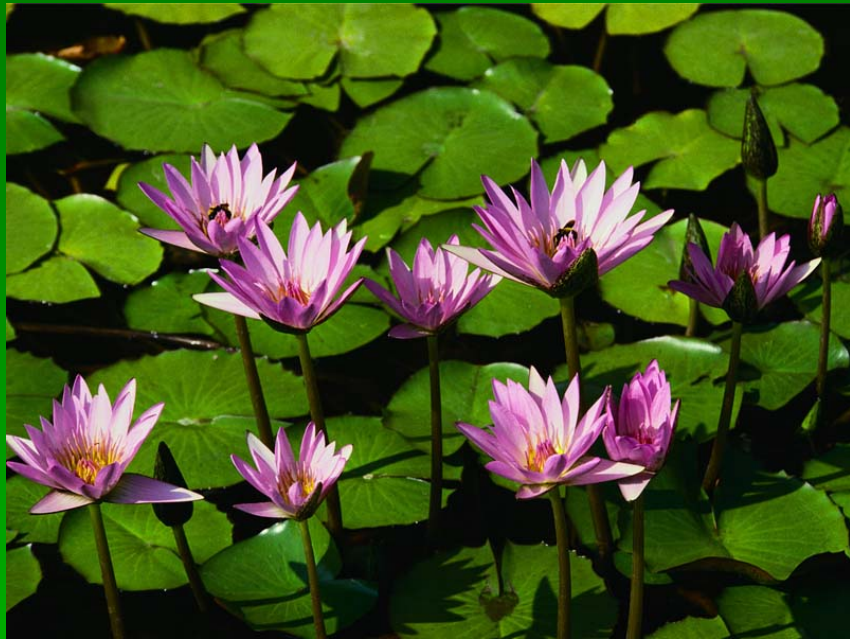
UVO cleaning method

- Photosensitized oxidation process
- The contaminants are excited and dissociated by the absorption of short-wavelength UV radiation

- Applications
 - Substrate cleaning prior to thin film deposition
 - Cleaning of silicon wafers, lenses, solar panels, and GaAs wafers
 - Etching Teflon and other organic materials
 - Improve adhesion of coatings on plastics
 - Increase hydrophilicity of surface



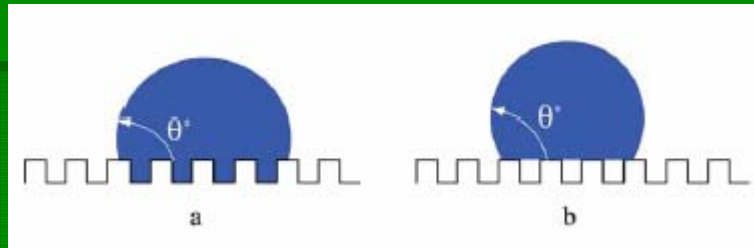
4. Lotus effect



Langmuir 2004, 20, 2405–2408

Superhydrophobic

초소수성 조건



Wenzel state

Cassie state

$$\cos \theta^* = r \cos \theta$$

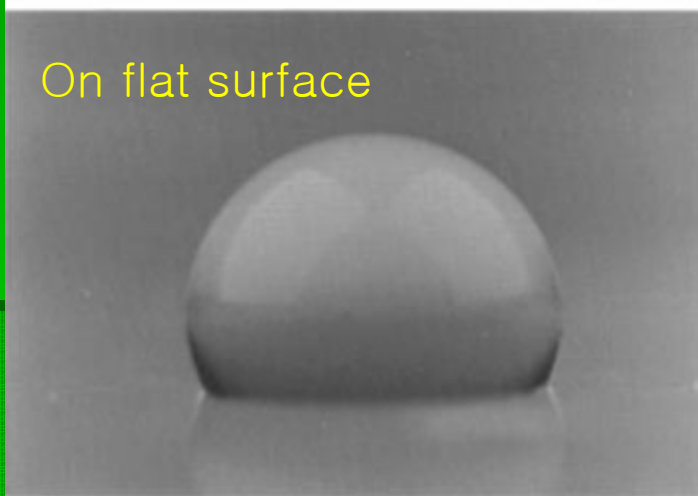
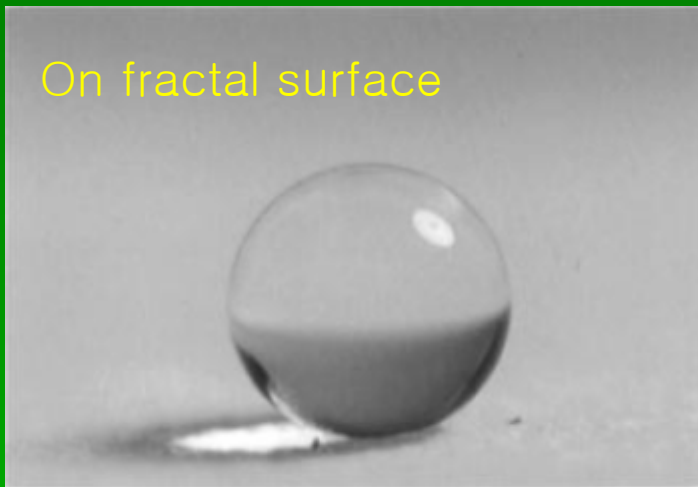
$$\cos \theta^* = -1 + \phi_s (\cos \theta + 1)$$

1. 접촉면이 작아야 한다.
2. Aspect ratio 가 크면 유리.
3. 표면에너지가 낮아야 한다.
4. 마이크로/나노 복합구조.



Super-Water-Repellent Fractal Surfaces

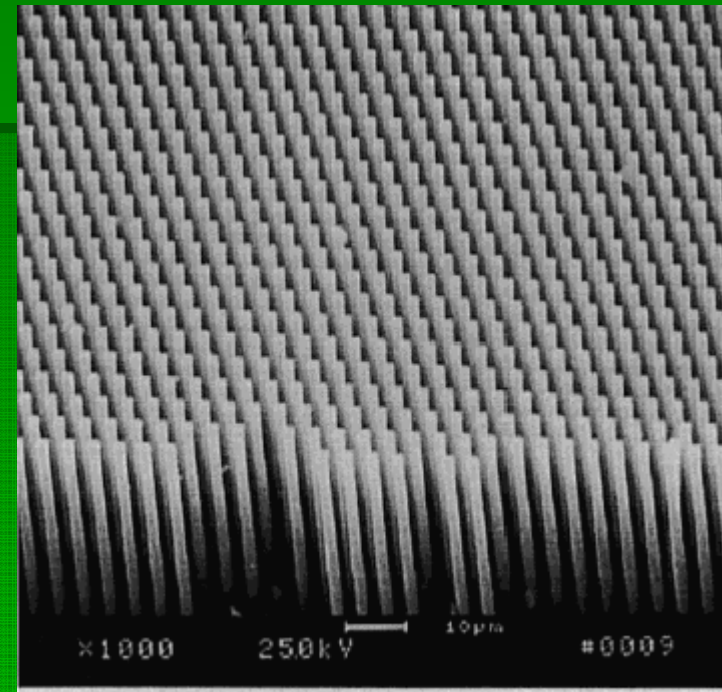
T. Onda,^{*,†} S. Shibuichi,[†] N. Satoh,[‡] and K. Tsujii[†]



Langmuir 2000, 16, 7777–7782

Ultrahydrophobic Surfaces. Effects of Topography Length Scales on Wettability

Didem Öner and Thomas J. McCarthy*

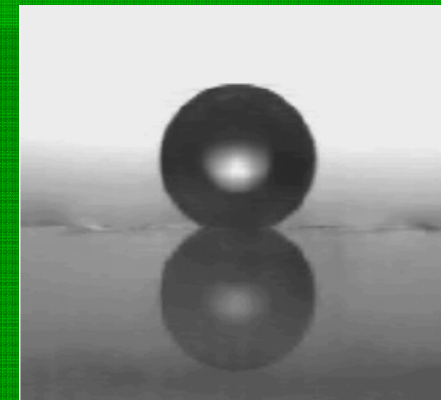
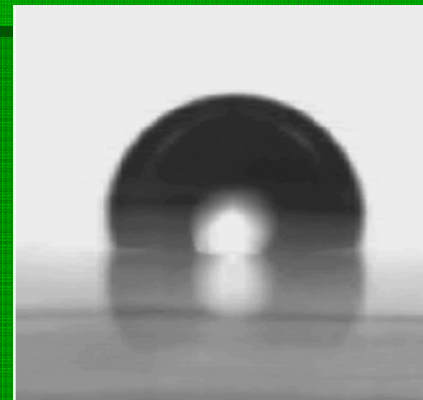
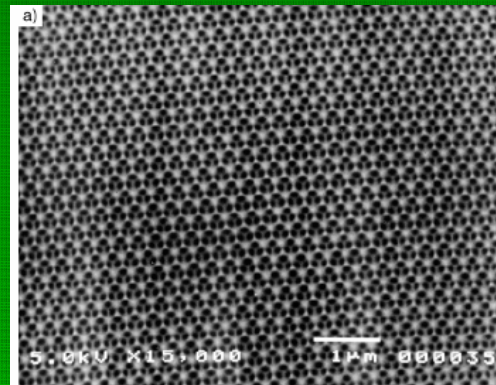
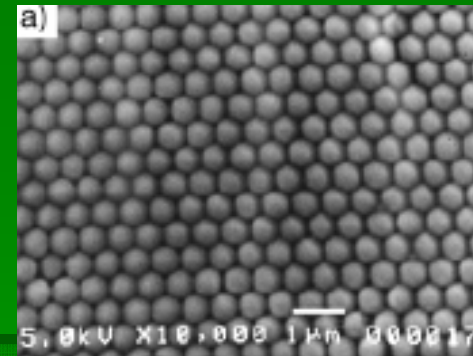
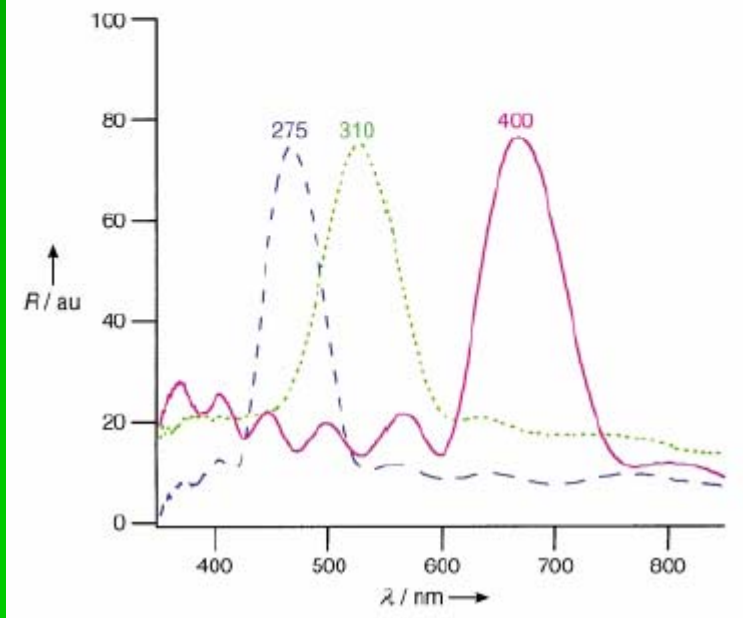
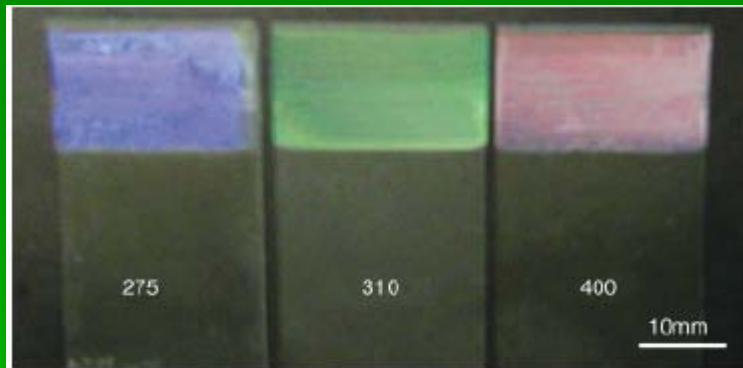


silicon surface	DMDCS-modified		ODMCS-modified		FDDCS-modified	
	θ_A (deg)	θ_R (deg)	θ_A (deg)	θ_R (deg)	θ_A (deg)	θ_R (deg)
smooth	107	102	102	94	119	110
2 $\mu\text{mSP}40\mu\text{m}$	176	141	174	141	170	146
8 $\mu\text{mSP}40\mu\text{m}$	173	134	173	139	170	140
16 $\mu\text{mSP}40\mu\text{m}$	171	144	174	134	168	145
32 $\mu\text{mSP}40\mu\text{m}$	168	142	170	132	170	146
64 $\mu\text{mSP}40\mu\text{m}$	139	81	114	65	149	100
128 $\mu\text{mSP}40\mu\text{m}$	116	80	95	58	131	93

Surface Effects from Nanostructure

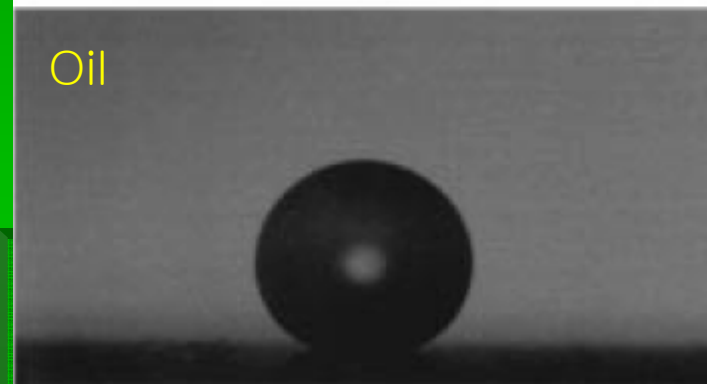
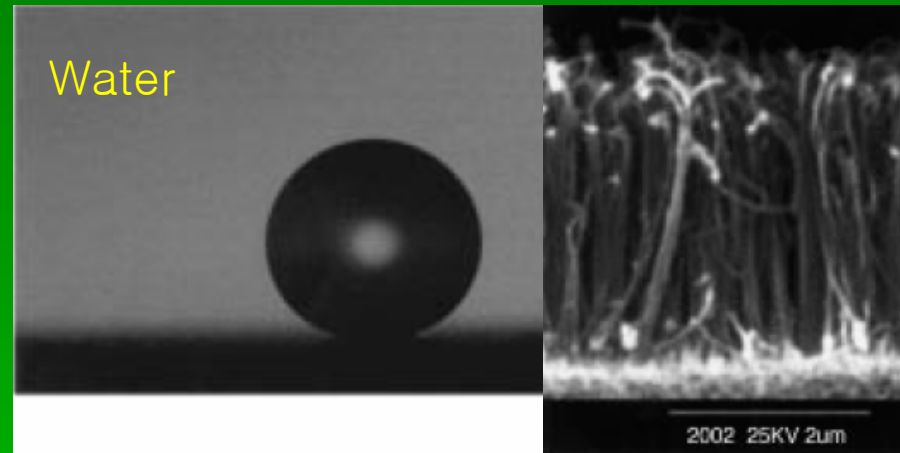
Structural Color and the Lotus Effect**

Zhong-Ze Gu, Hiroshi Uetsuka, Kazuyuki Takahashi,
Rie Nakajima, Hiroshi Onishi, Akira Fujishima, and
Osamu Sato*



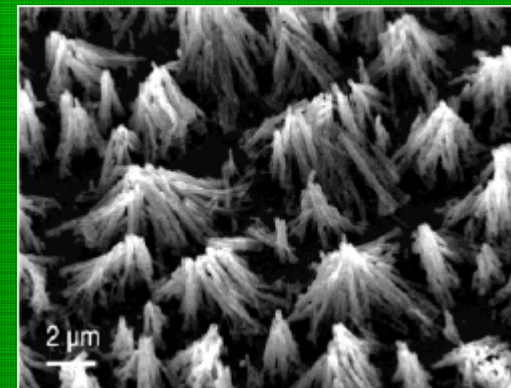
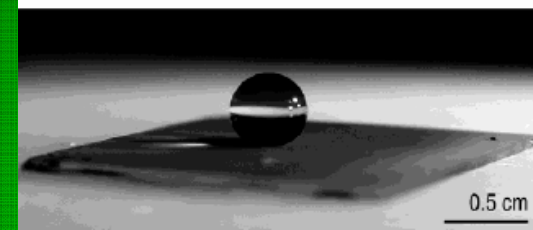
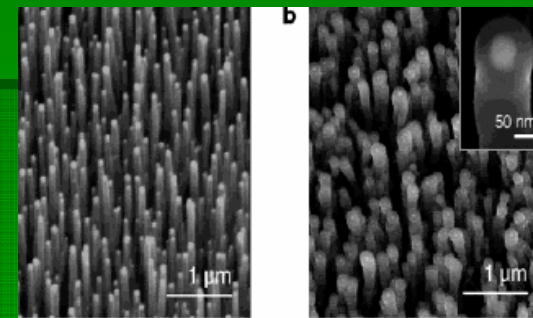
Super-“Amphiphobic” Aligned Carbon Nanotube Films**

Huanjun Li, Xianbao Wang, Yanlin Song, Yunqi Liu, Qianshu Li, Lei Jiang,* and Daoben Zhu



Superhydrophobic Carbon Nanotube Forests

Kenneth K. S. Lau,^{*,†} José Bico,[‡] Kenneth B. K. Teo,[§] Manish Chhowalla,^{||} Gehan A. J. Amaratunga,[§] William I. Milne,[§] Gareth H. McKinley,[‡] and Karen K. Gleason[†]



Reversible Super-hydrophobicity to Super-hydrophilicity Transition of Aligned ZnO Nanorod Films

Xinjian Feng, Lin Feng, Meihua Jin, Jin Zhai, Lei Jiang,* and Daoben Zhu

