IN THE NAME OF GOD

BY:S.MA.SH

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SELF-CLEANING COATINGS

By
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Instructor
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April 2021

Outline

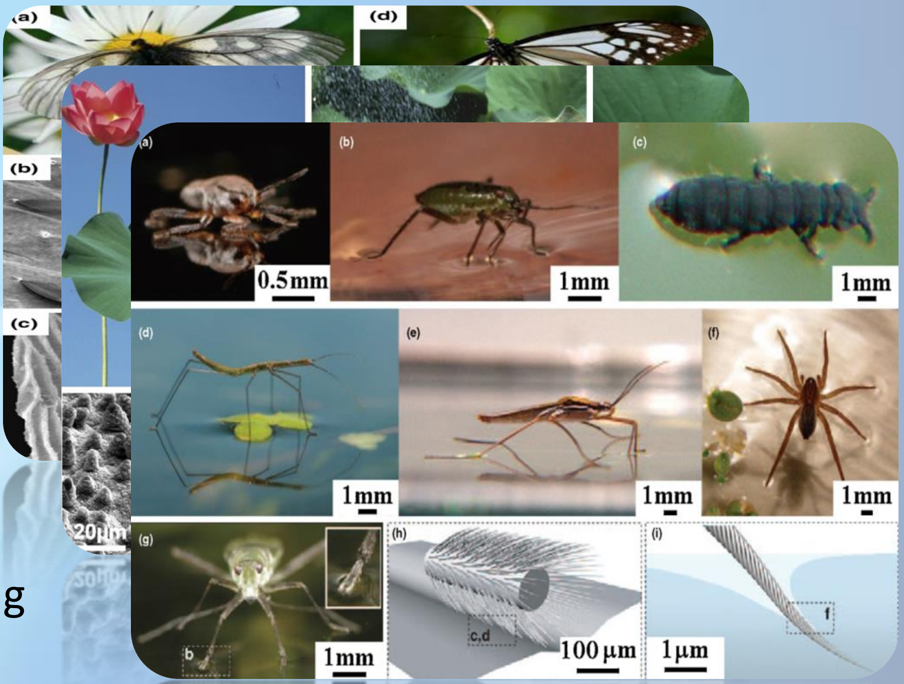
- Introduction
- Self-Cleaning Effect
- Types of Surfaces
- Applications
- Conclusion
- References

Introduction

❖The Inspiration of Nature:self-cleaning process

Transparent butterfly wings of Parnassius glacialis and a white translucent of Parantica sita

Lotus leaf is the best example of self cleaning surfaces



(a–f) Images of different water-walking arthropods; (g–i) images of a leg at different magnifications

Introduction

Applications:

Window glasses

Solar panels

Textile industry

Purposes:

Reduce maintenance costs
Increase the time needed to keeping equipment clean
Increase durability

Introduction

Self-cleaning coatings categories:

1. Hydrophilic self-cleaning coatings

   Water is spread over the surface

   It can carry and eliminate dirt and contaminants

   The advantage:

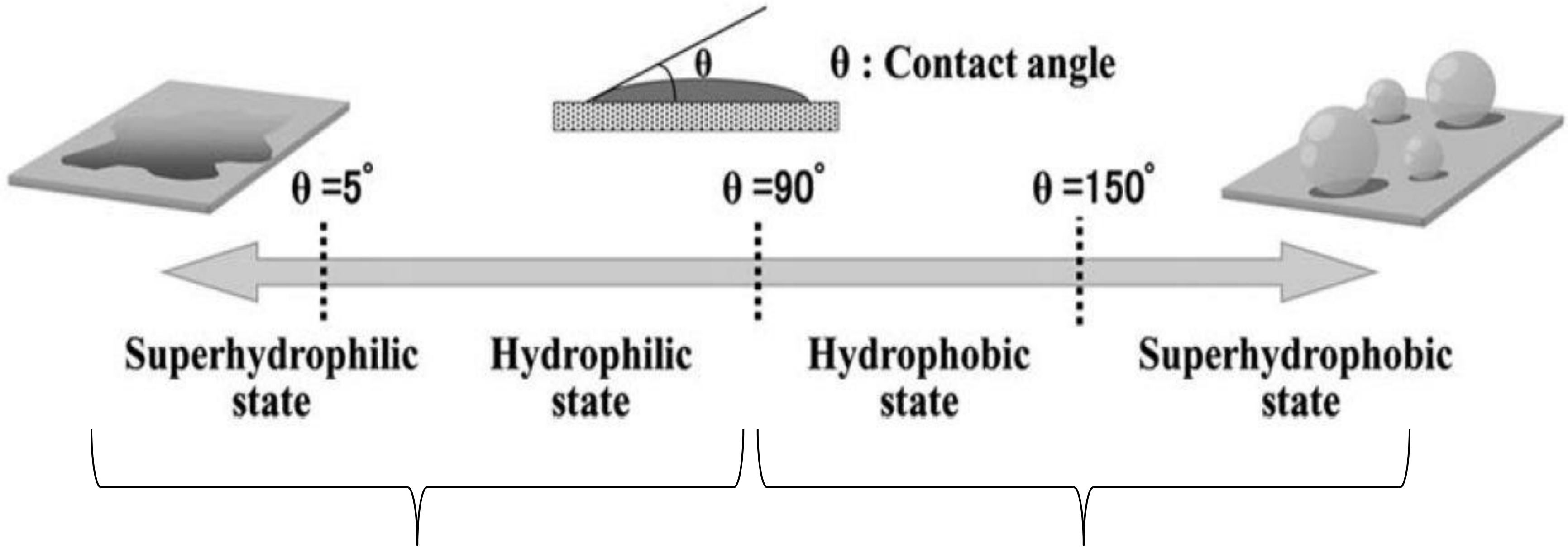
   Using of appropriate metal oxides→ by the sunlight→ The destruction of the chemical structure of contaminants

2. Hydrophobic self-cleaning coatings

   Droplets of water glides on the surface and clean it

Self-Cleaning Effect

Depending on Contact angle with three phase interfaces (solid-liquid-gas)



Very high surface energy

Very low surface energy

How measure the angle of contact ?

For smooth surface “Young Equation”:

When a liquid drop is placed in contact with a solid, the equilibrium of the solid and liquid surfaces will be established at a certain angle called the static contact angle CA, Θ, given by the Young equation:

$$\cos\theta = \frac{\gamma_{\mathrm{SG}} - \gamma_{\mathrm{SL}}}{\gamma_{\mathrm{LG}}}$$

where γ_{SG}, γ_{SL} and γ_{LG} are the surface energies of the solid against air, solid against liquid and liquid against air, respectively.

How measure the angle of contact ?

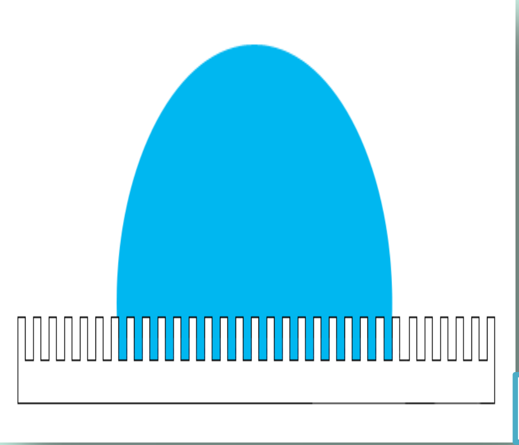
Wenzel model:

He modified the Young equation as follows:

$$\cos\theta^{*} = r\left(\frac{\gamma_{SG}-\gamma_{SL}}{\gamma_{LG}}\right) = r\cos\theta$$

Where, r is the non-dimensional surface roughness factor, defined by the equation , ratio of the actual area of a rough surface, A_{SL}, to its flat projected area, A_f .

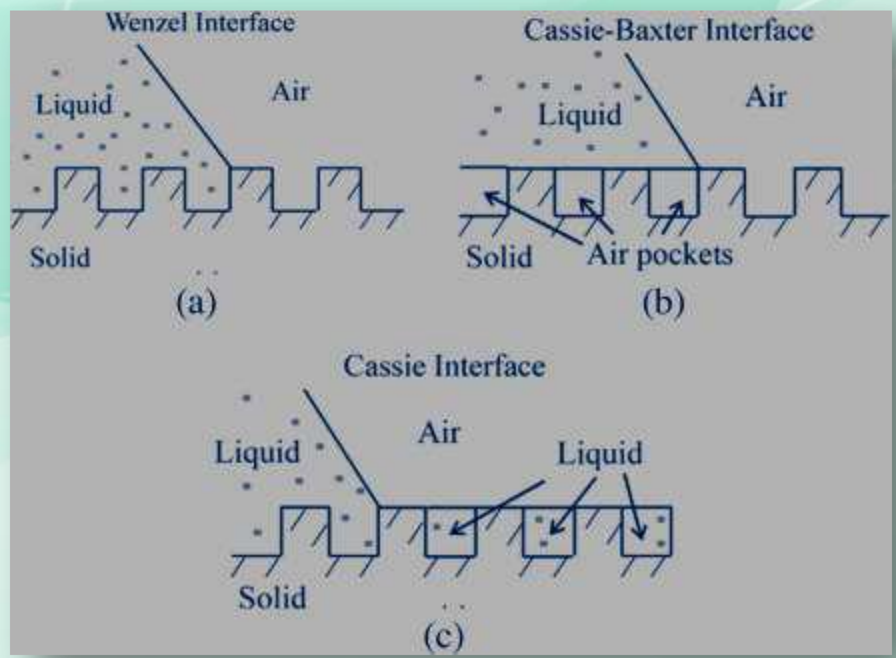
$$r = \frac{A_{sl}}{A_f}$$



How measure the angle of contact ?

Cassie-Baxter:

Model for heterogeneous surfaces composed of two fractions, one with a fractional area f_1 and contact angle θ_1 and the other with f_2 and θ_2, with $f_1 + f_2 = 1$.
The contact angle is thus given by equation: $\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2$



How measure the angle of contact ?

Cassie-Baxter:

A special case of this model

Show that θ^* is depended on the percentage of the solid that is in contact with droplet

$\emptyset_s$=% of solid

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

If $\emptyset_s \rightarrow 0 \Rightarrow$ the droplet sitted on more air

$\Rightarrow \cos\theta^* \rightarrow -1$

$\Rightarrow \theta^* \rightarrow 180^o$

Types of surfaces

Hydrophilic and superhydrophilic surfaces

Hydrophilic surfaces destroy the chemical structure of contaminants in the present of sunlight (photocatalysis)

↓

inspired from the photosynthesis

In 2001 The first group of self-cleaning coatings that were used commercially

These glasses were made of thin and transparent titanium dioxide

It cleanses through two separate mechanisms, photocatalysis and hydrophilicity

PILKINGTON

Hydrophilic and superhydrophilic surfaces

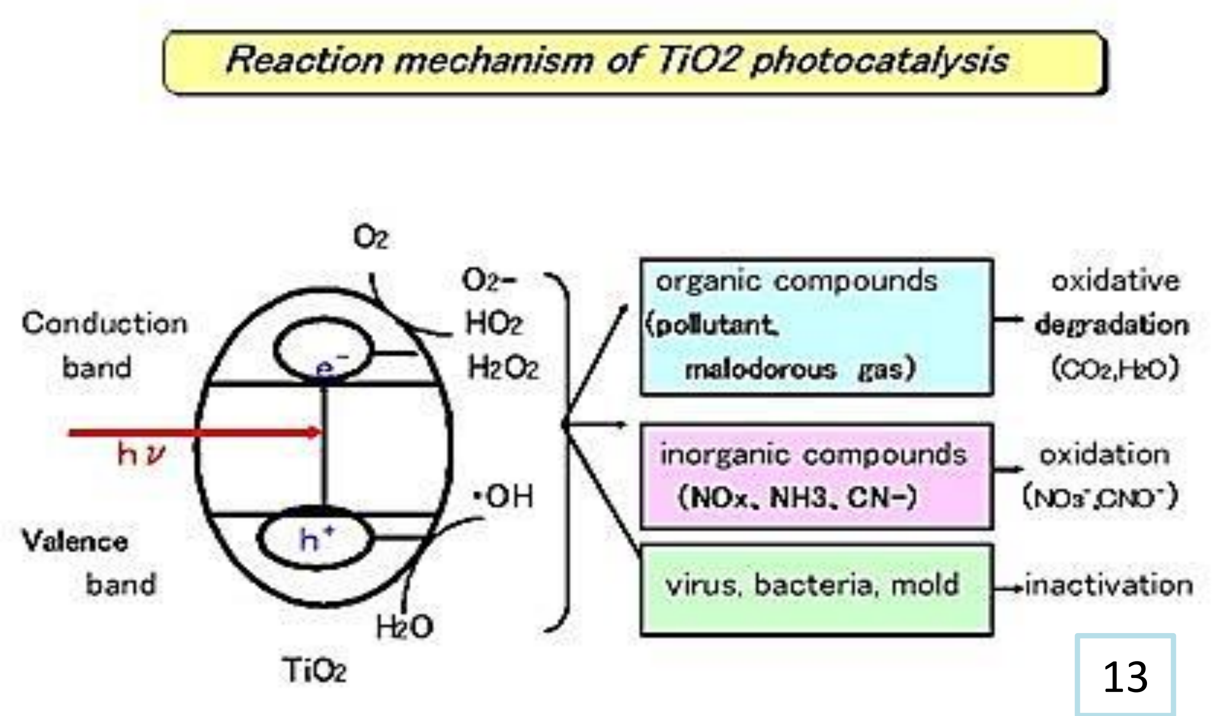
During the photocatalysis process:

The chemical structure of organic pollutants and other impurities on the coating is broken down by absorbing sunlight

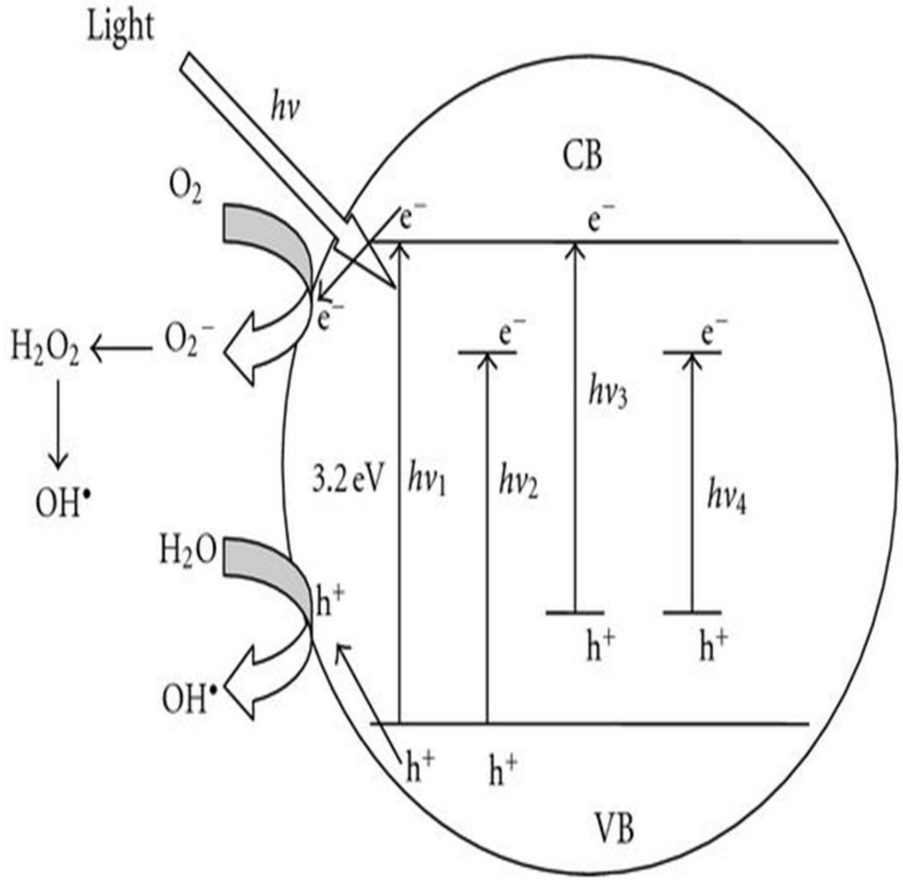
The surface hydrophilicity also reduces the contact angle

layers of water are covered on the surface that eliminates contamination

In normal conditions:



Hydrophilic and superhydrophilic surfaces



Scheme 1: Schematic representation of the mechanism of photocatalytic titanium dioxide particles (TiO_2: hv_1, Fe-TiO_2: hv_2, N-TiO_2: hv_3, Fe-N-TiO_2: hv_4).

Hydrophilic and superhydrophilic surfaces

Titanium dioxide superhydrophilicity

induced by sunlight

Holes that are caused by optical stimulation in titanium dioxide
Takes electron from O_2 on the surface and leading to oxidized form of O_2

FreeRadical oxygen is created on the surface, which allows hydrogen bonding

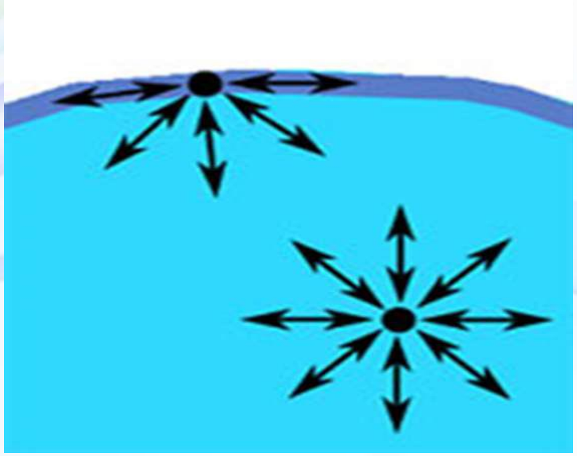
By forming a bond between oxygen and hydrogen radicals, hydroxide groups are formed on the surface that reduce the contact angle.

Other self-cleaning surfaces: ZrO_2 , ZnO , CdS , WO_3

Hydrophilic and superhydrophilic surfaces

Since the surface properties of the material is defferent from its bulk

Because atoms and molecules adjacent to the material's surface are less bonded to the atoms in the substance and are thermodynamically more unstable



This instability increases the energy of matter

Levels of energy are quantizatized in the surface
while within the material, these levels become compressed and create a band structure of energy

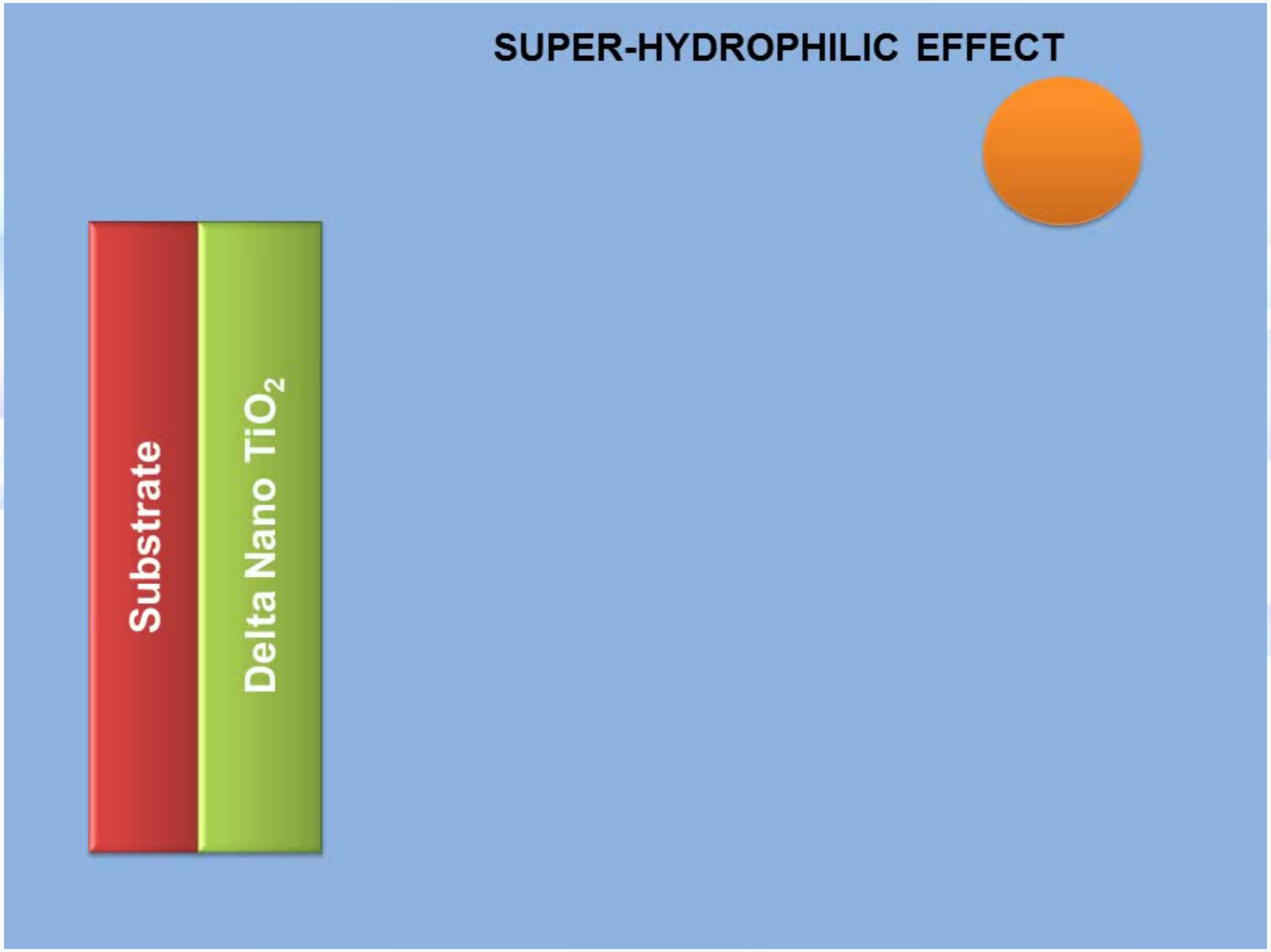
Hydrophilic and superhydrophilic surfaces

In the nanoscale, the surface-to-volume ratio increases, and the possibility of creating holes in the surface and decomposition of the chemical composition of contaminants increases.

For this reason, Titanium dioxide nanoparticles are commonly used as superhydrophilicity surfaces.

By reducing the particle size, the percentage of photocatalytic activity increases

Hydrophilic and superhydrophilic surfaces



Types of surfaces

Hydrophobic and superhydrophobic coatings

Ward and colleagues observed for the first time that the lotus leaf was completely clean in the swamps and that no contamination was observed.

In the 1960s, studies done by scanning electron microscopy (SEM) showed that surfaces that are completely smooth in macroscopic look are rough in microscopic scale

When a surface has a texture in a micrometer or nanometer scale, the interface between air and water increases in a drop that is placed on the surface, and the capillary strength between the droplets and the surface is severely reduced.

Hydrophobic and superhydrophobic coatings

Therefore, the drop of water forms a spherical shape and flows freely and particles of pollution and dust are connected to it

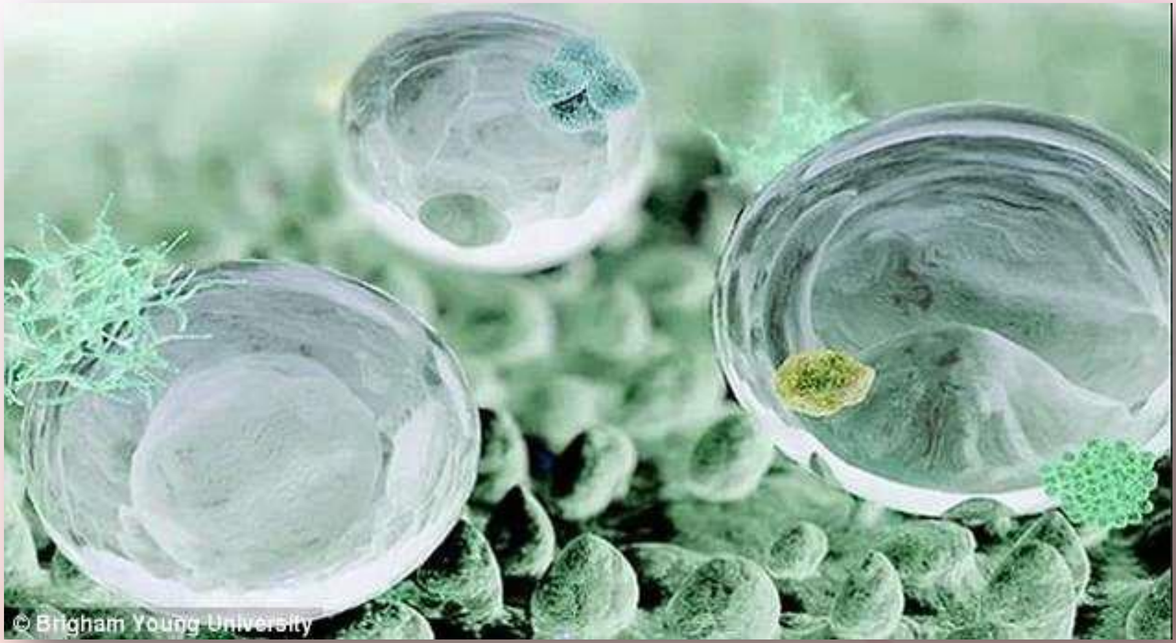
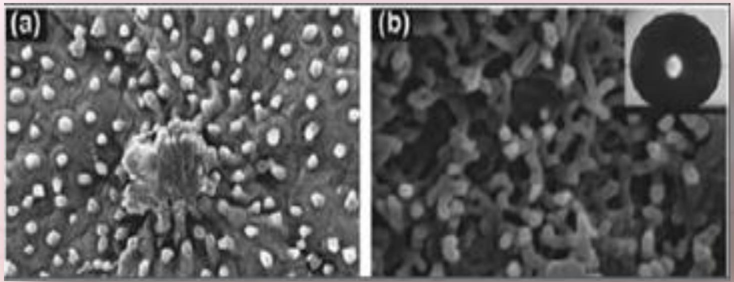


Image of a droplets of water on a lotus leaf; contaminants stick to the water droplet and detach from the surface

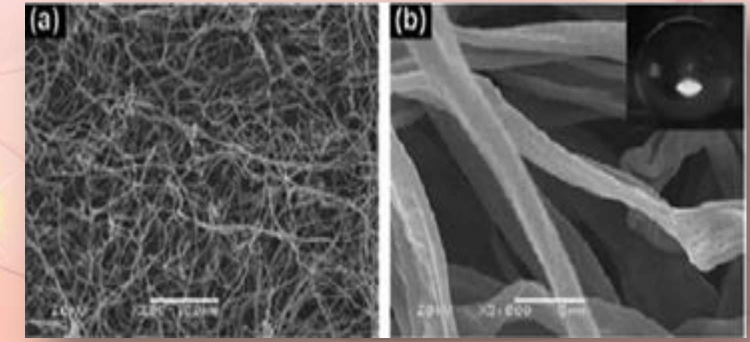
Hydrophobic and superhydrophobic coatings

The results of research by Guo and colleagues showed that there are two categories of surface microstructure in the leaves of the trees:

Hierarchical micro and nano structures : The lotus leaf in figure has a hierarchical structure The leaves of this plant have grooves of 3 to 10 µm in size, and particles in a size of 100 nm are spread across the grooves.



Unitary fine lines structures: the figure is image of the back of a ramee with a smooth structure, in which fibers with a diameter of 1 to 2 micrometers are seen across the surface.



Hydrophobic and superhydrophobic coatings

Developing methods for superhydrophobe surfaces preparation by imitation of existing surfaces in nature

Many researchers around the world have tried to produce surfaces that have very low surface energy and can control surface micro-level and nanoscale morphology, and thus reach a superhydrophobe surface.

Research shows that it is almost impossible to create a contact angle of more than 120 degrees on a flat surface, only by relying on the hydrophobic chemical structure of that surface, without any tissue in the micro or nanoscale.

Hydrophobic and superhydrophobic coatings

Therefore, to create superhydrophobe surface, there must be two surface roughness and a hydrophobic chemical structure (low surface energy)

The contact angle of the water at the surfaces with low energy increases with increasing porosity and surface roughness.

The effect of surface roughness can be expressed with the aid of the Wenzel equation

The Wensel equation predicts that if the molecular level is rough, it shows more hydrophobia.

Hydrophobic and superhydrophobic coatings

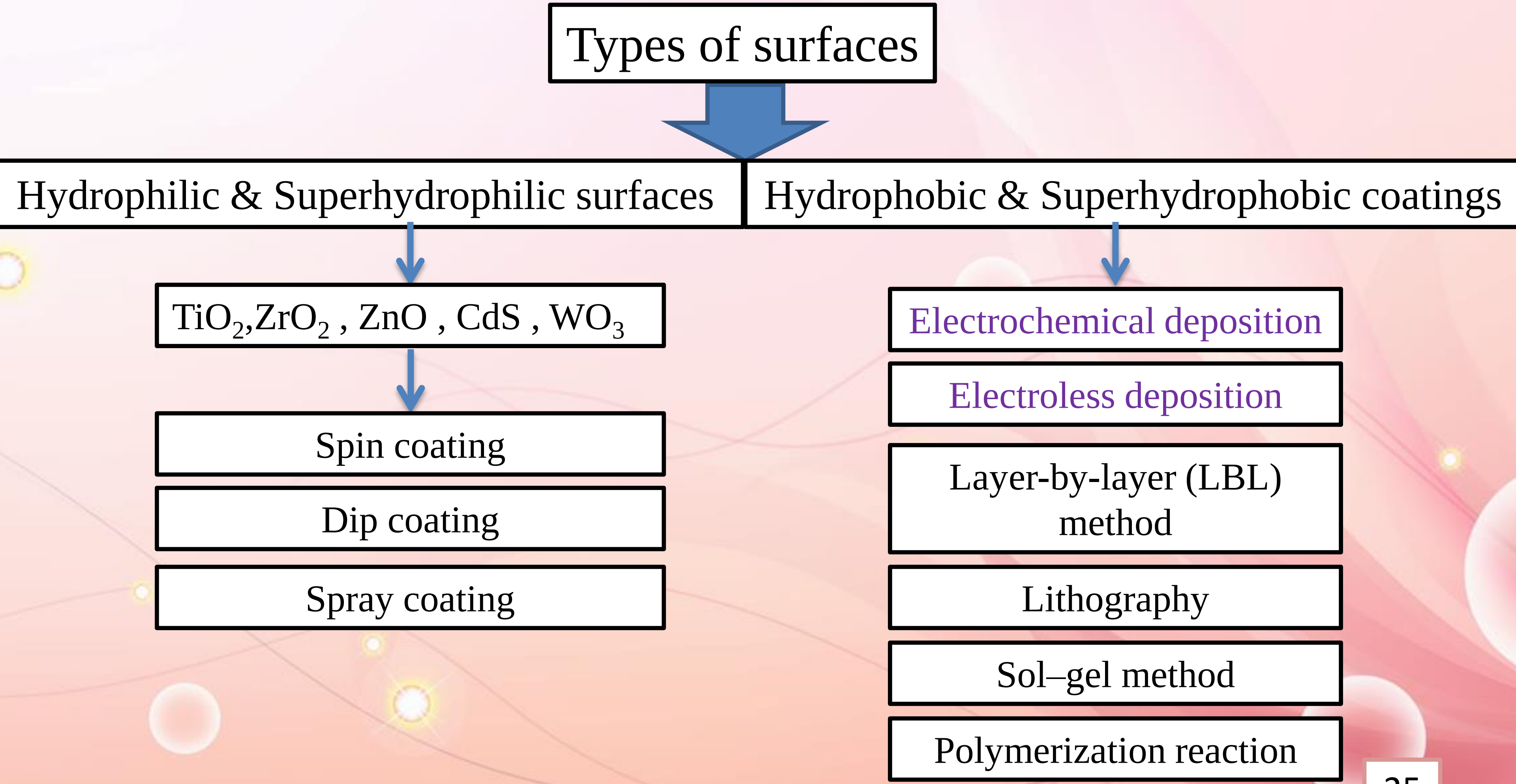
The methods used to fabricate hydrophobic and superhydrophobic surfaces can be divided into two general categories:

1. Fabricate a rough surface from a low surface energy material

2. Modifying a rough surface with a low surface energy material

Generally, the combination of the two methods is commonly used to create such surfaces.

Fabrication of Self-Cleaning Surfaces



Types of surfaces

- Hydrophilic & Superhydrophilic surfaces
  - TiO_2, ZrO_2 , ZnO , CdS , WO_3
    - Spin coating
    - Dip coating
    - Spray coating
- Hydrophobic & Superhydrophobic coatings
  - Electrochemical deposition
  - Electroless deposition
  - Layer-by-layer (LBL) method
  - Lithography
  - Sol–gel method
  - Polymerization reaction

Surface & Coatings Technology 204 (2010) 2483–2486

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

One-step fabrication process of superhydrophobic green coatings

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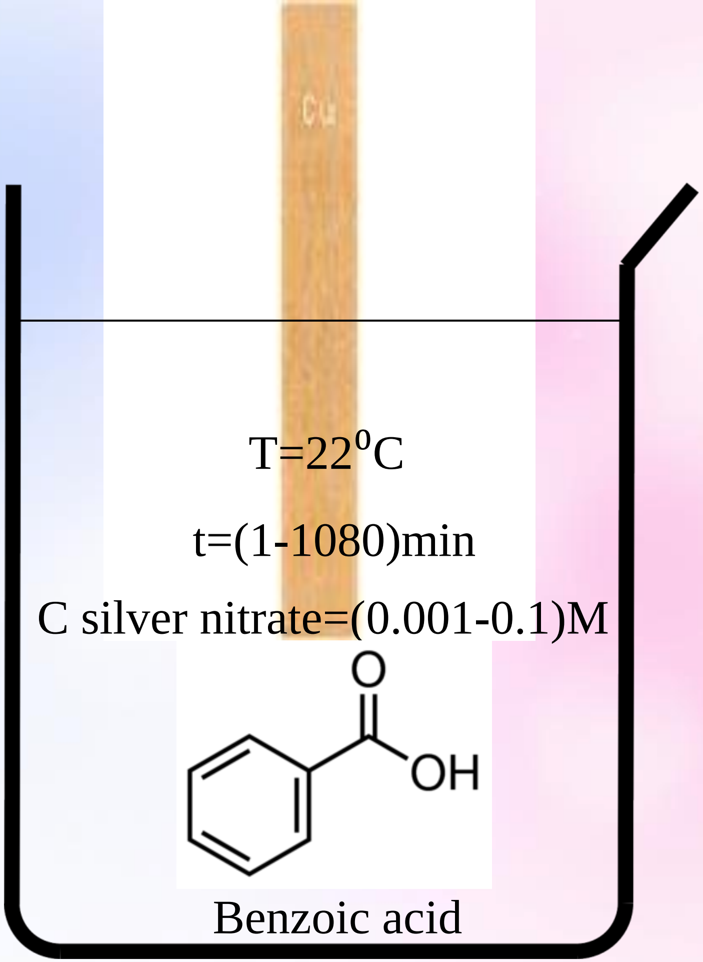
Electroless deposition

Experimental :



T=22^{0}C

t=(1-1080)min

C silver nitrate=(0.001-0.1)M

Benzoic acid

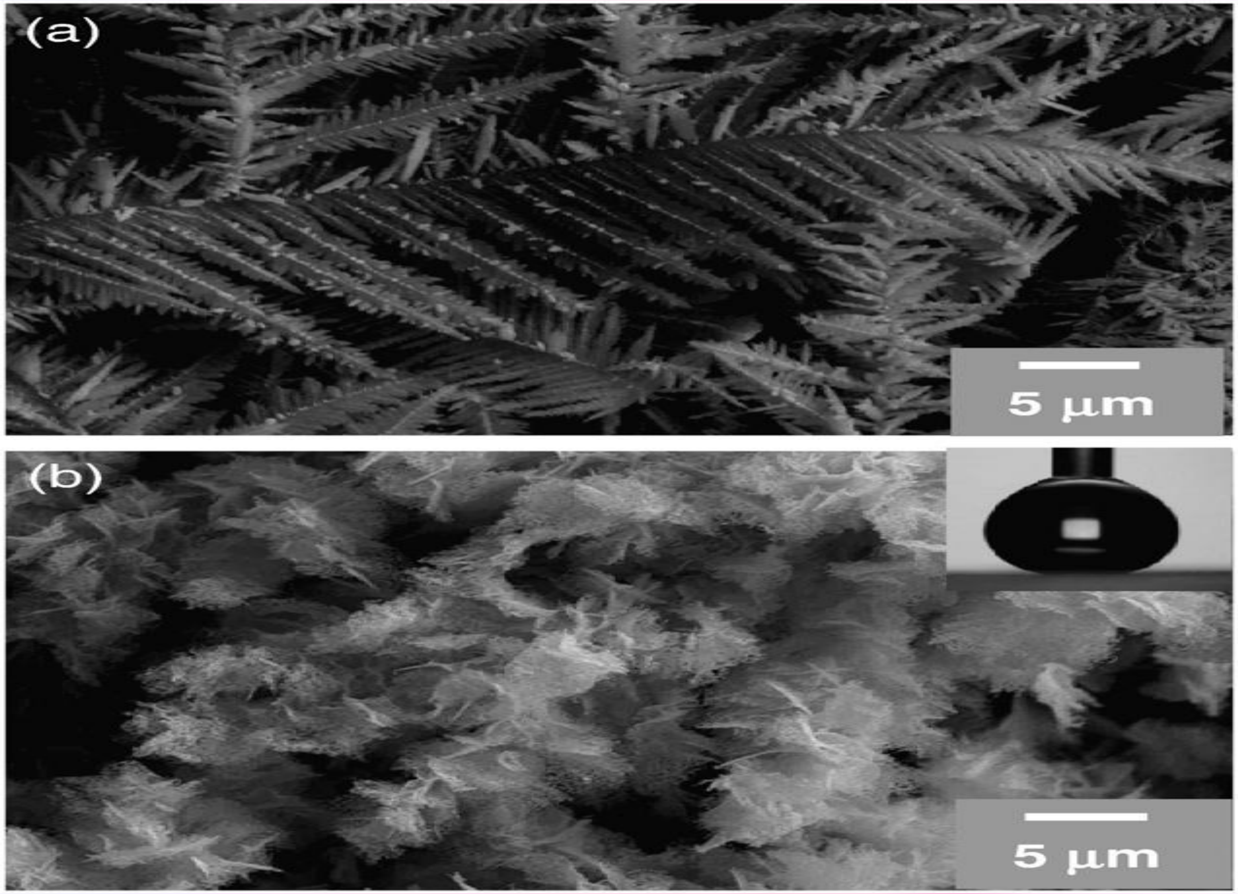
And

T=22^{0}C

t=(1-1080)min

C silver nitrate=(0.001-0.1)M

Electroless deposition

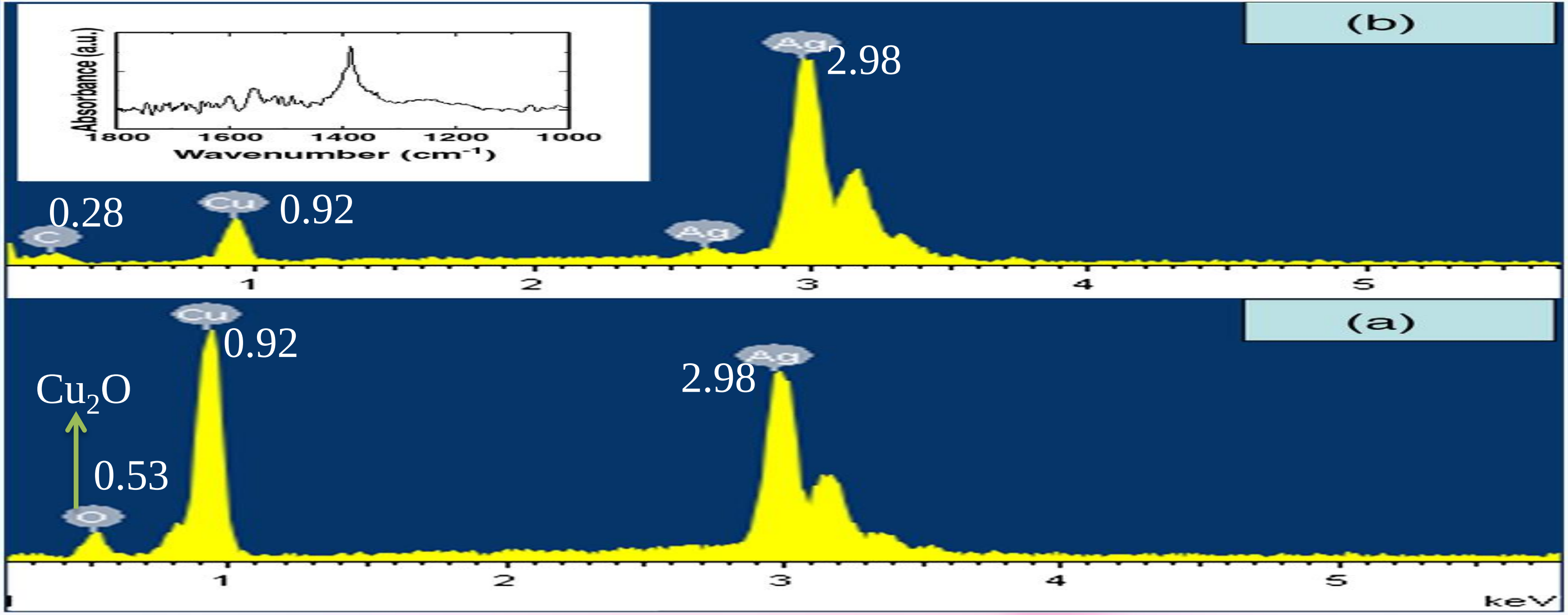


The water contact angle (CA) ~162°

SEM images of silver films deposited on copper substrates by galvanic exchange reaction in the silver nitrate solution: (a) leaf-like surface morphology without benzoic acid and (b) flower-like structure (composed of micro-nano patterned)with benzoic acid. Inset shows the drop of 8µl water on the silver surface prepared with benzoic acid molecules.

Electroless deposition

The high water contact angle and water repellency is attributed to
1.the rough flower-like morphological features of this film
2.the low surface energy of benzoic acid incorporated into these films
The low surface energy of benzoic acid arises from the presence of the low surface energy –CH groups in the benzoic acid



EDX spectra of silver films prepared in (a) silver nitrate solution and (b) silver nitrate solution with benzoic acid molecules. Inset shows the FTIR spectra of silver powder collected from the silver films prepared with the benzoic acid molecules.

Surface & Coatings Technology 231 (2013) 88–92

Contents lists available at ScienceDirect

Surface & Coatings Technology

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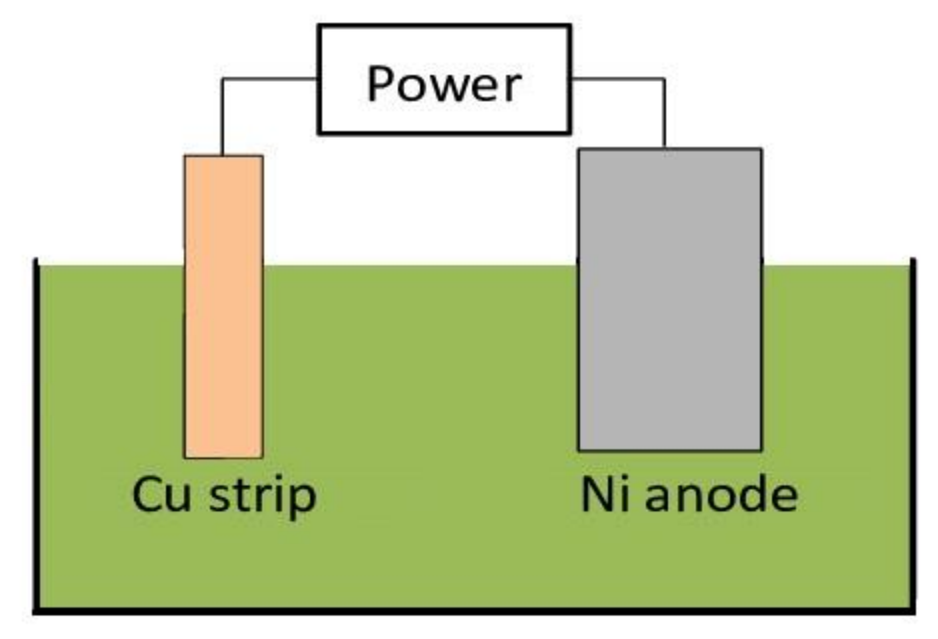
A facile process for preparing superhydrophobic nickel films with stearic acid

Zhuo Chen [1], Feifei Tian [2], Anmin Hu [*], Ming Li [3]

The State Key Laboratory of the Metal Matrix Composites, Key Laboratory for Thin Film and Microfabrication Technology of the Ministry of Education, Shanghai Jiao Tong University, No. 800, Dongchuan Road, 200240, Shanghai, P.R. China

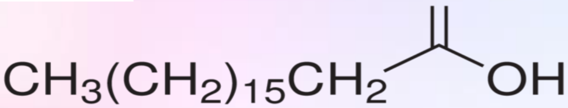
Electrochemical deposition

Nickel surface with nanocone array structure was fabricated by electrodeposition



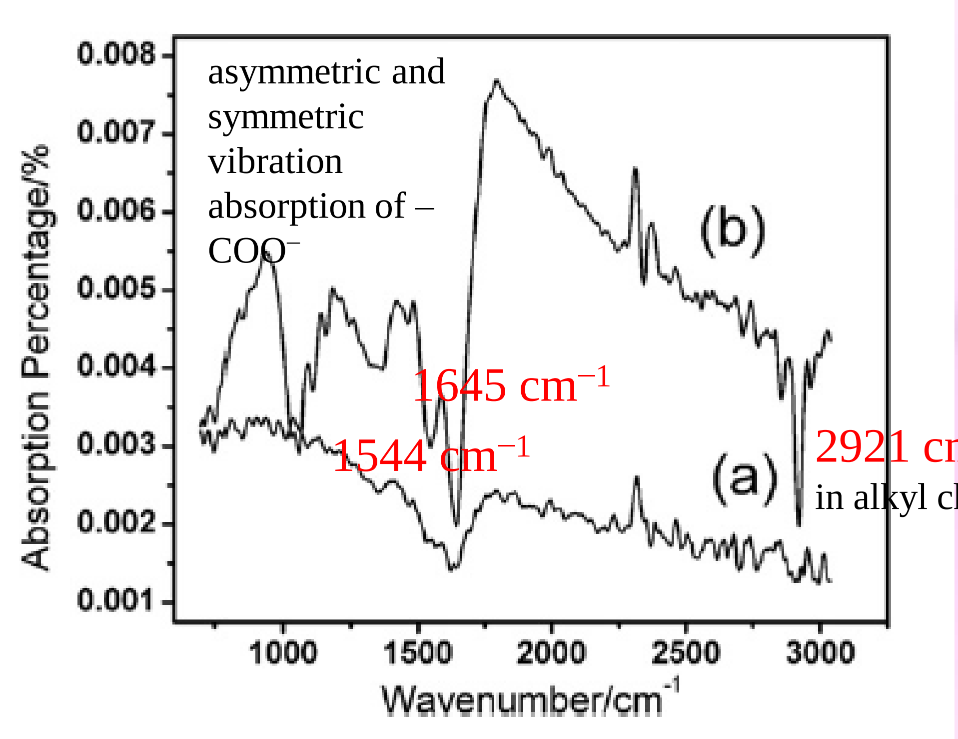
1.5mol/L ethylenediamine dihydrochloride
as a crystal modifier

1 mol/L $NiCl_2 \cdot 6H_2O$
0.5 mol/L H_3BO_3
3.5 mmol/L Stearic acid in ethanol as surface modifier
T=60 °C
pH=4.0
Current density=2 A/dm^2 and t=8 min



$CH_3(CH_2)_{15}CH_2COOH$

Electrochemical deposition



asymmetric and symmetric vibration absorption of –COO$^-$

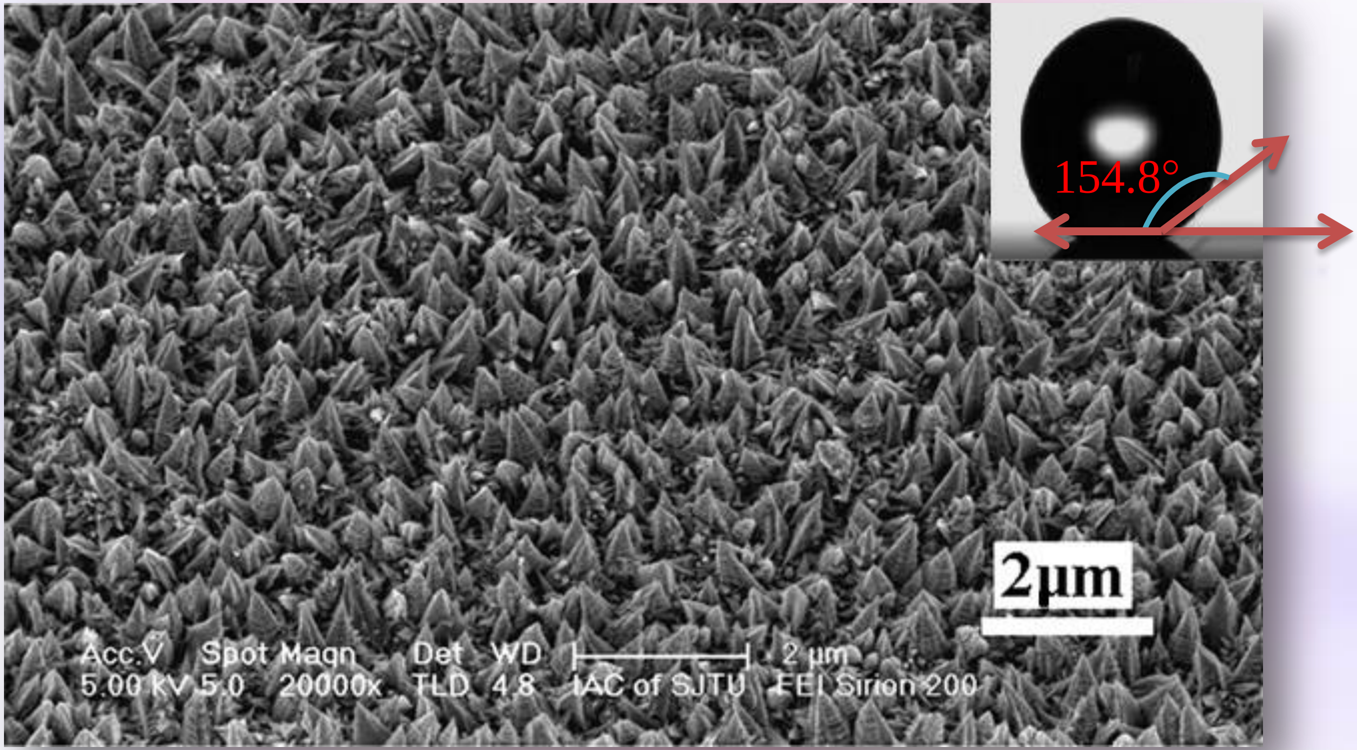
1645 cm^{-1}

1544 cm^{-1}

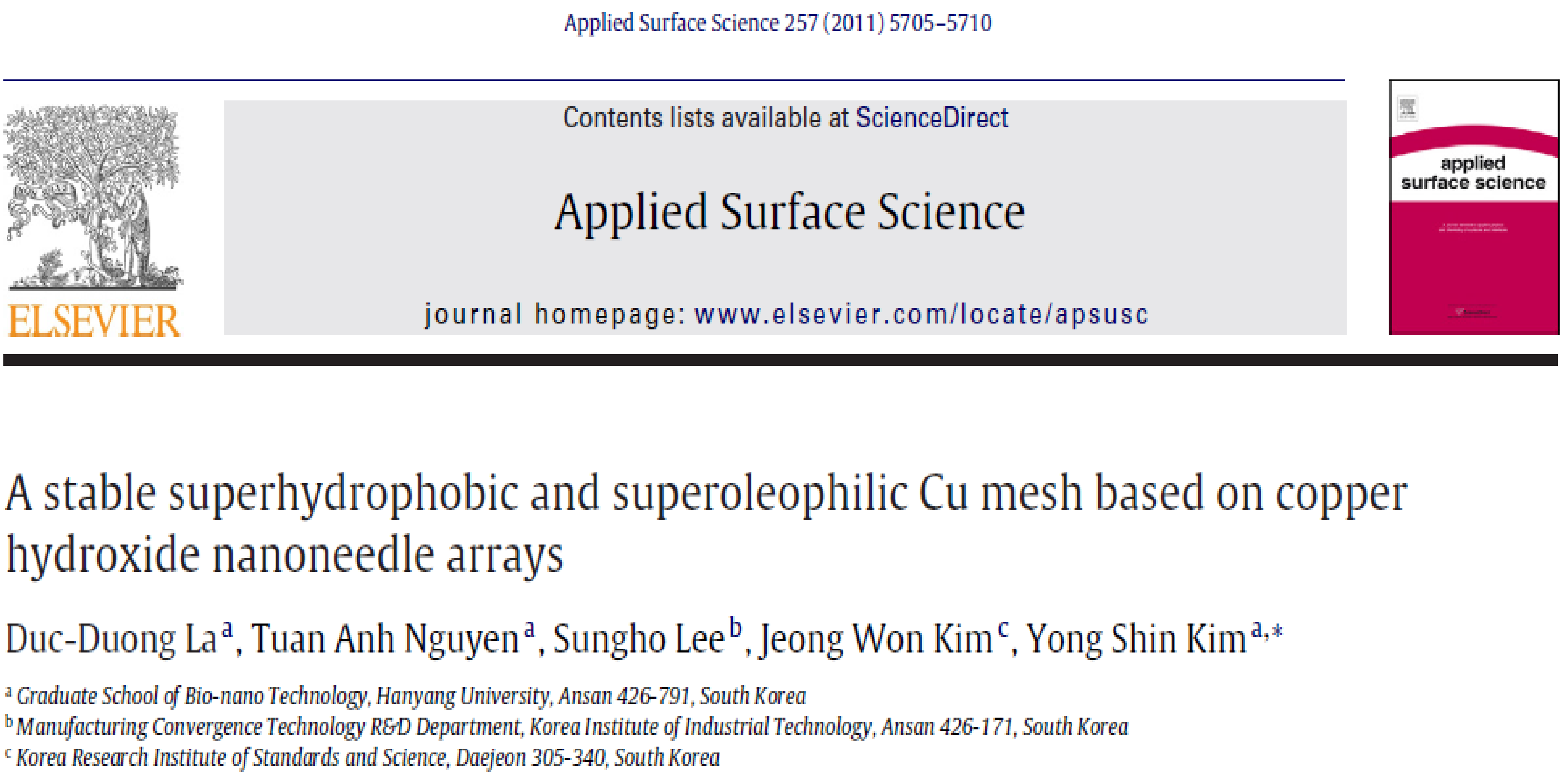
2921 cm^{-1} C-H vibration in alkyl chains

Fig. 2. FTIR-ATR spectra of nickel surfaces fabricated at 2 A/dm^2 for 8 min (a) before modification, (b) after modification with stearic acid.

Electrochemical deposition



SEM images of nickel nanocone arrays
water contact angle was 154.8° and the sliding angle of 4.7°



Applied Surface Science 257 (2011) 5705–5710

Contents lists available at ScienceDirect

Applied Surface Science

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A stable superhydrophobic and superoleophilic Cu mesh based on copper hydroxide nanoneedle arrays

Duc-Duong La[a], Tuan Anh Nguyen[a], Sungho Lee[b], Jeong Won Kim[c], Yong Shin Kim[a,*]

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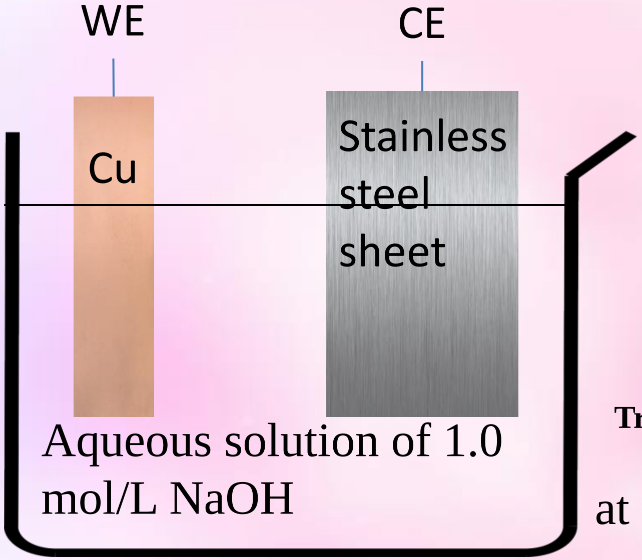
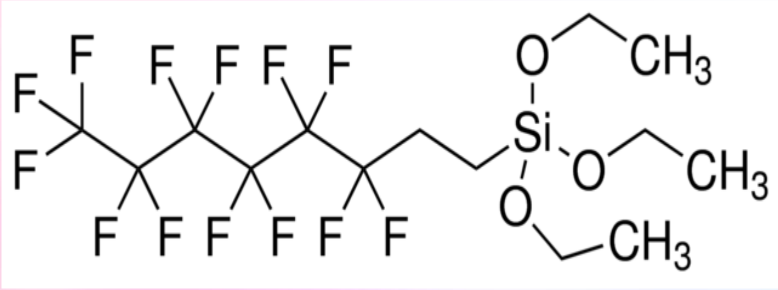
[b] *Manufacturing Convergence Technology R&D Department, Korea Institute of Industrial Technology, Ansan 426-171, South Korea*
[c] *Korea Research Institute of Standards and Science, Daejeon 305-340, South Korea*

Electrochemical deposition





Triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octyl)silane

at room temperature

$Cu(OH)_2$ films were electrochemically grown at a constant current density of $2 mA/cm^2$ with a typical reaction time of 600 s

Rinsed twice with DI water and then dried in air

The silanization process

Surface modification was performed by dipping samples into an ethanol solution of 0.5% 1H,1H,2H,2H-perfluorooctyltriethoxysilane for 24 h

Followed by washing with ethanol and drying in an oven at 120 °C for 1 h

FAS-modified $Cu(OH)_2$ nanoneedles

Electrochemical deposition

The formation of $Cu(OH)_2$ nanoneedles was previously interpreted with an electrochemical oxidation process:

$Cu(s) \rightarrow Cu(s)^{2+} + 2e^{-}$ and $Cu(s)^{2+} + 2OH(aq)^{-} \rightarrow Cu(OH)_2(s)$

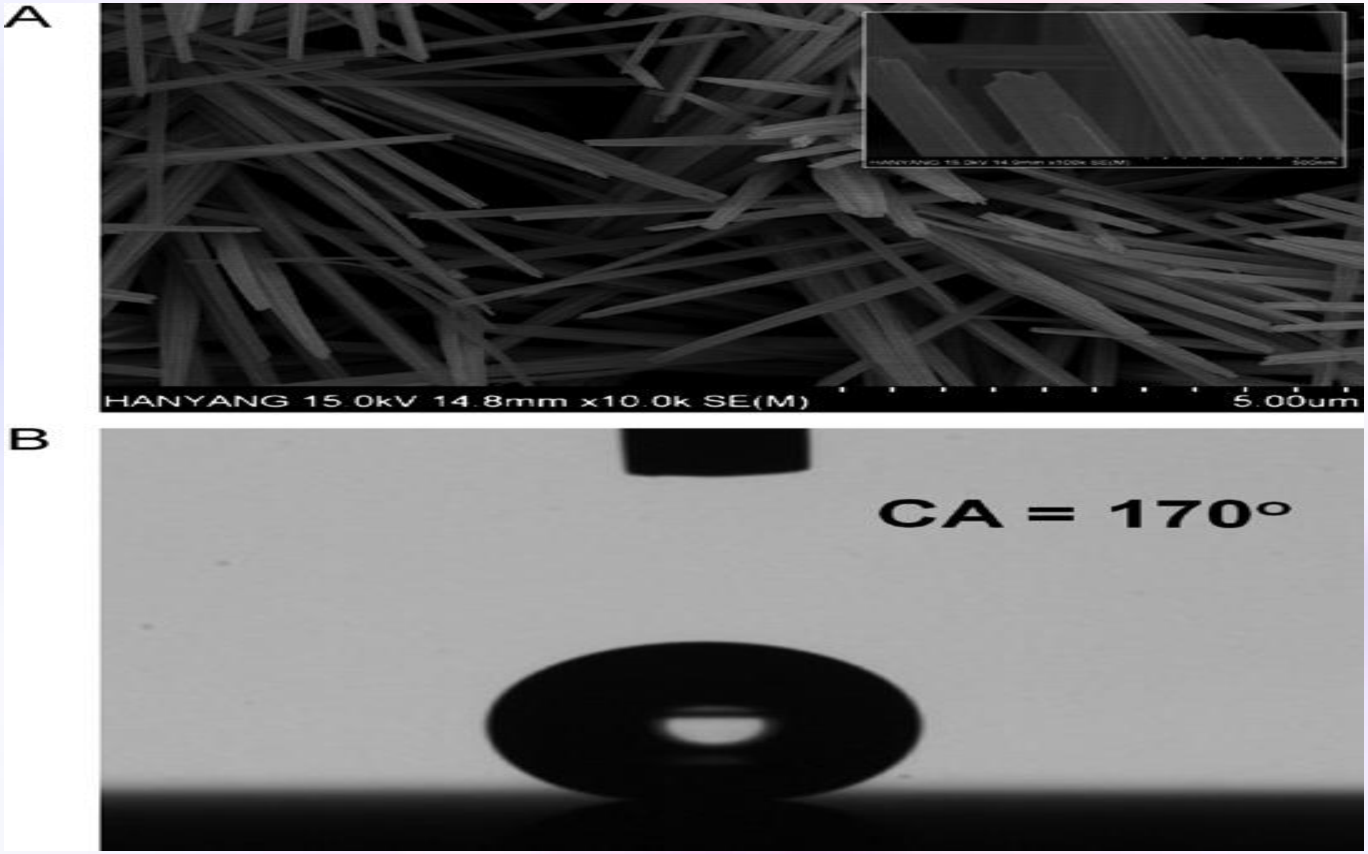
these results indicated that orthorhombic $Cu(OH)_2$ nanoneedle arrays were uniformly produced over a large area through electrochemical anodization

Unmodified $Cu(OH)_2$ nanoneedle films were observed to have a very low CA close to 0° due to hydrophilic OH functional groups

The CA of FAS-modified samples promptly increased and then reached a steady-state value around 170° after 2 h while the Si content gradually increased as silanization time increased

Slide angle is less than 5°

Electrochemical deposition



(A) An SEM image of FAS-modified Cu$(OH)_2$ nanoneedle arrays and (B) a cross-sectional optical image of a water droplet on the modified surface.

Applications

Self-cleaning surfaces are used in a variety of fields:

Textile industry(Self-cleaning clothes)

Automotive industry(Self-cleaning glasses, car body, and mirrors)

Optical industries(Cameras, sensors, lenses, telescopes)

Shipbuilding industry(Anticorrosive coatings)

Windows

Paints

Solar panels

Applications

Self-cleaning commercial products:

The Pilkington Group has commercialized a self-cleaning glass for the first time

PILKINGTON

The German lotus company(Lotusan) produces self-cleaning paints

Cardinal glass industry in Europe and Saint-Gobain

Cardinal®
Glass Industries Inc.

SAINT-GOBAIN

PPG industry

PPG Commercial Performance Coatings

Pittsburgh Plate Glass Company (1883–1968)

Conclusion

Self-cleaning coatings technology used to:

Increase durability

Reduction in costs

Reduce the time needed to maintain equipment

Dividing into two categories with the relative similar set up to Prevent Sediment Pollutions They are used as coverings on different surfaces

Applications in various fields such as:

Textile industry

Automotive industry

Aircraft industry

Optical industries

Many commercial products have come into production using this technology

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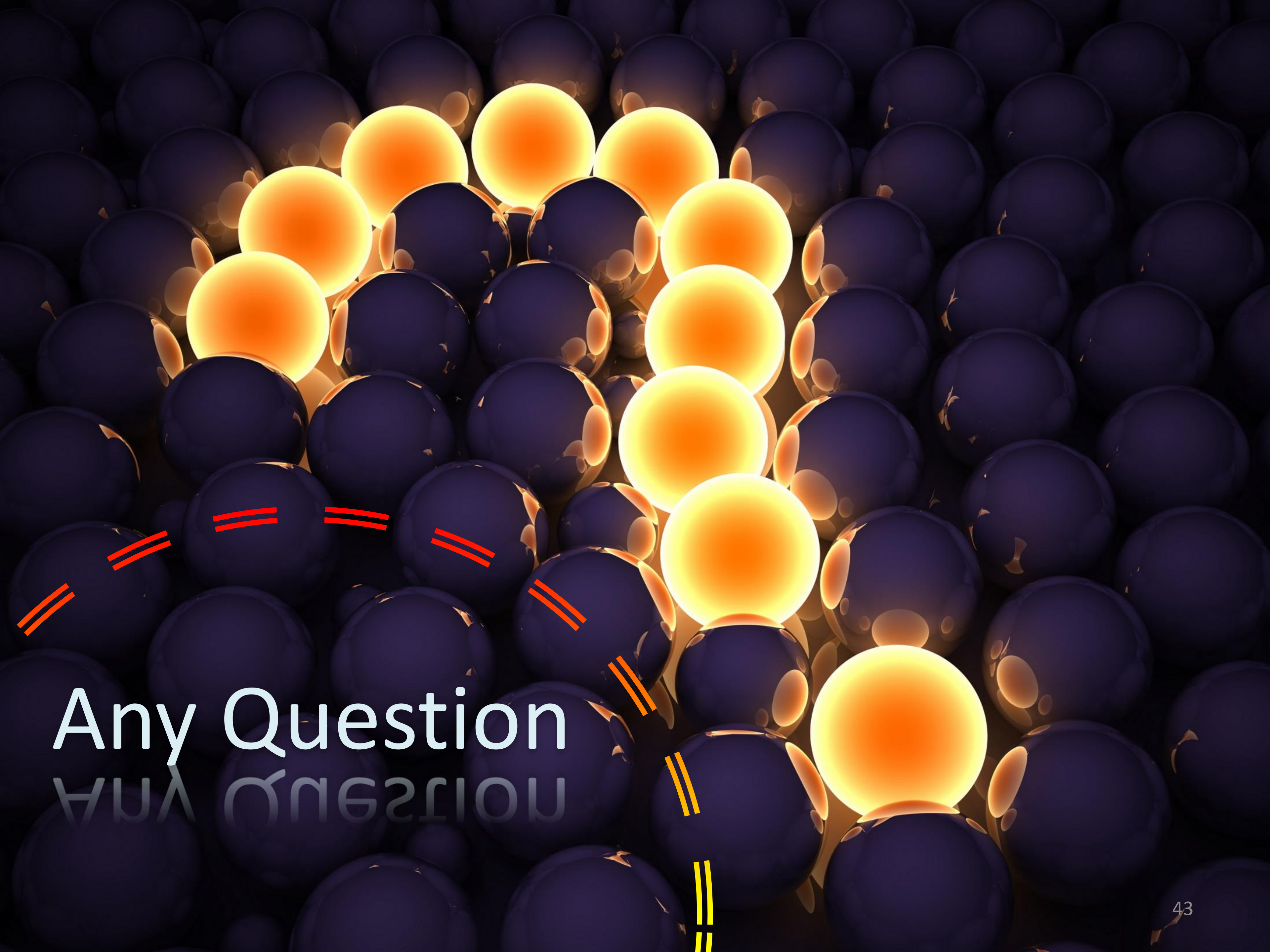
Thank you!



Any Question