Functionele eigenschappen van smeermiddel-geïmpregneerd geanodiseerd aluminium

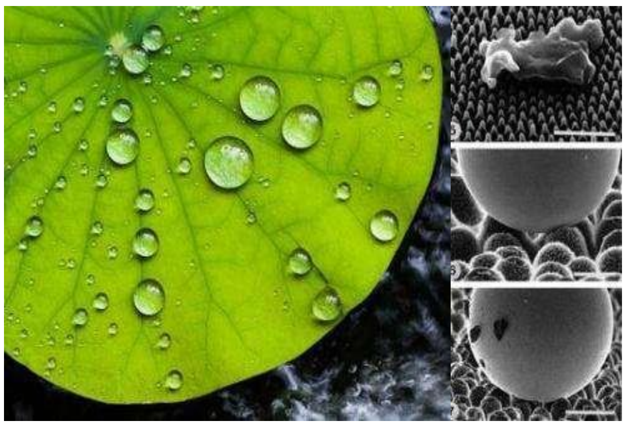
Arjan Mol

Dequan Wu, Lingwei Ma, Dawei Zhang, Badar Minhas, Bei Liu, Hongchang Qian, Herman Terryn, Xiaogang Li

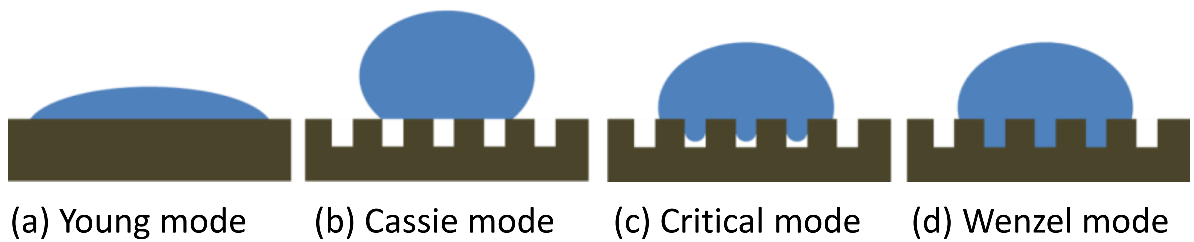
Superhydrophobicity

Lotus effect:

Inspired by the lotus leaves, superhydrophobic surfaces are specific rough substructures which are modified with low surface energy materials



lotus leaf superhydrophobic structure



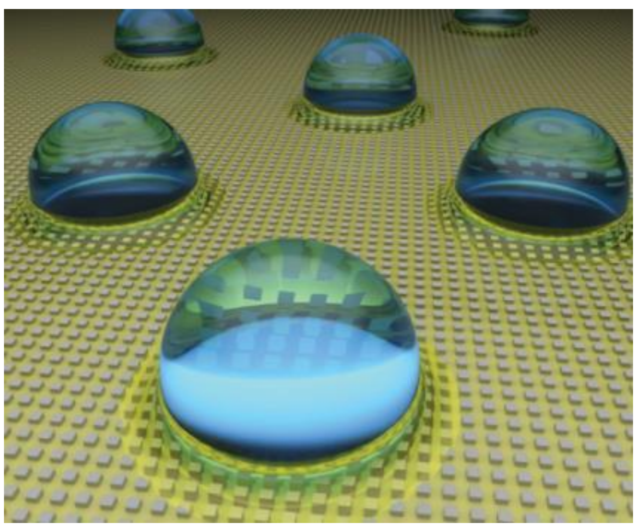
Cassie mode of superhydrophobic surfaces would transfer into Wenzel mode caused by the collapse of trapped air pockets under impact or during long time immersion.

Challenges for superhydrophobic surfaces

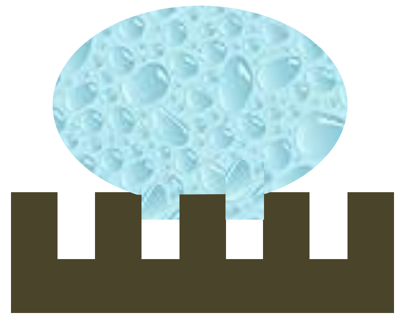
- Weak mechanical durability of delicate microstructures
- Instability of the solid-liquid interface and liquid–air surface

LIS/SLIPS

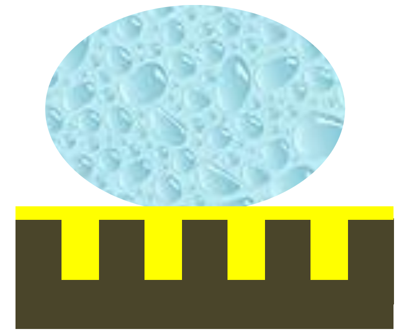
Nepenthes effect



smeermiddel-geïmpregneerd oppervlak



superhydrophobic surface



LIS/SLIPS surface

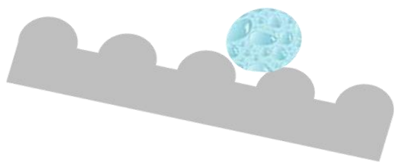
- **Replacing the air layer with lubricant film**, a lubricant infused surface (LIS), or slippery liquid-infused porous surface (SLIPS) can be created.
- The lubricant locked in the rough substrate can form a **continuous, homogenous, smooth and stable** liquid-solid interface.

Comparison

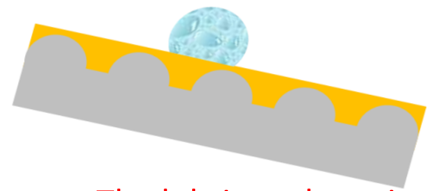
Superhydrophobic surface

LIS/SLIPS

1.

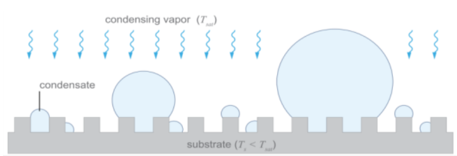


The droplet size must be in the scale of mm to be able to slide

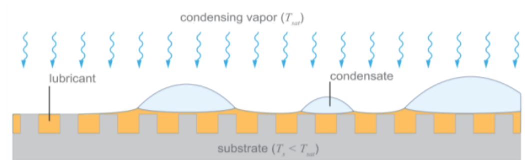


The lubricant layer is ultra smooth. Droplets with sizes > 20 microns can slide off and the sliding angle is much lower

2.

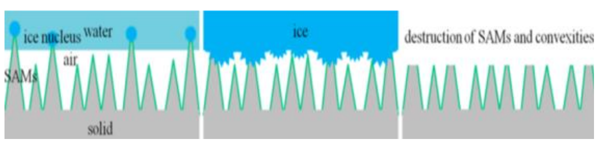


Moisture condensates in the rough microstructures

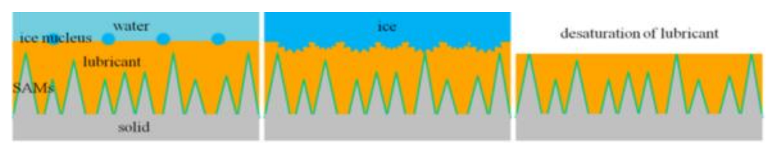


The lubricant layer itself is a good barrier

3.

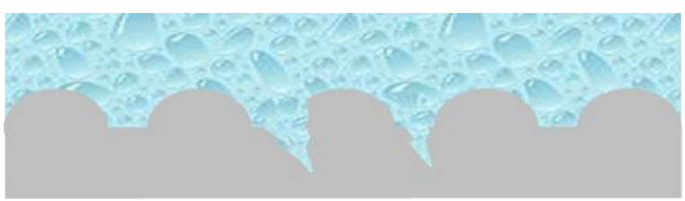


Ice nucleation and de-icing process damage the microstructure



No nucleation sites for ice

4.



Mechanical attacks may occur easily.

The lubricant serves as a good buffer, and it can flow to the damage zones instantaneously.

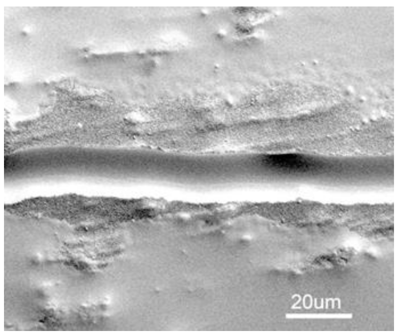
Application

Characterization of infused oil :

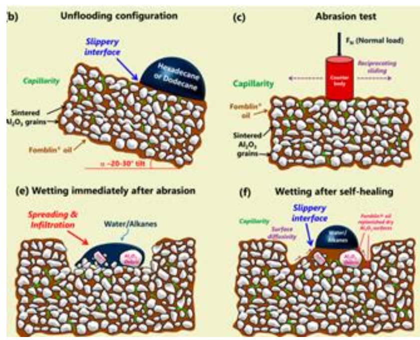
low surface energy, chemically inert, low viscosity, low evaporation,

Enabling a wide application of the LIS/SLIPS

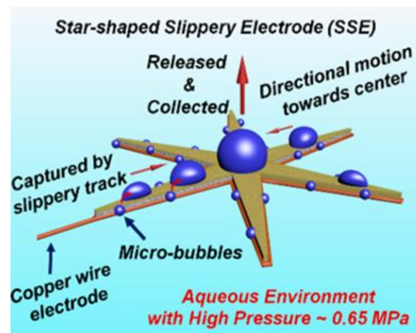
Self-healing



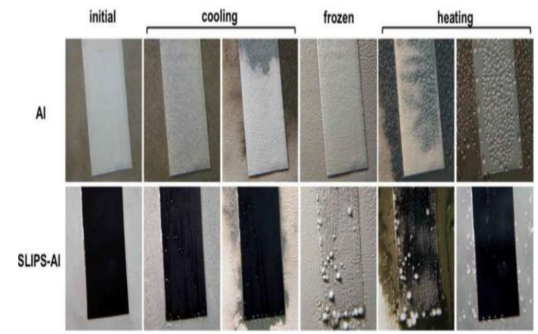
Wear resistant



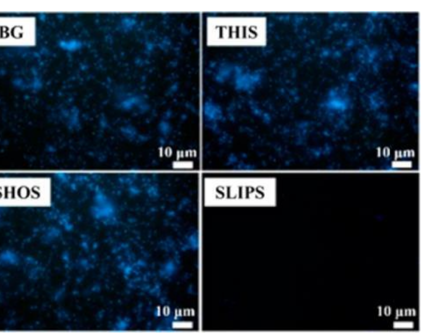
Fluidic control



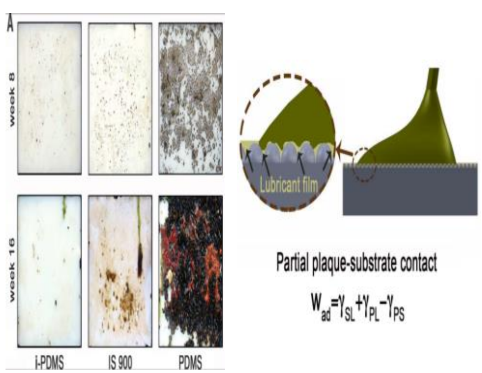
Anti-icing/fogging



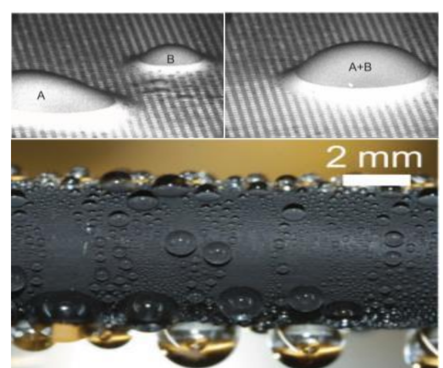
Anti-bacterial



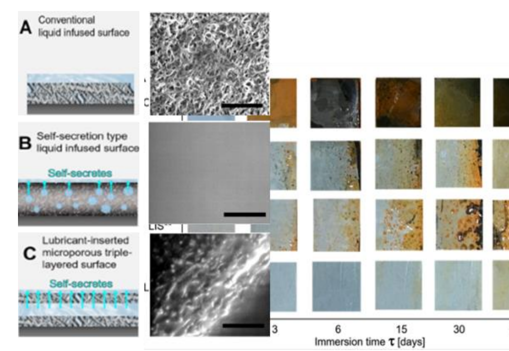
Anti-fouling



Anti-condensation



Anti-corrosion



Fabrication principle

Infusion

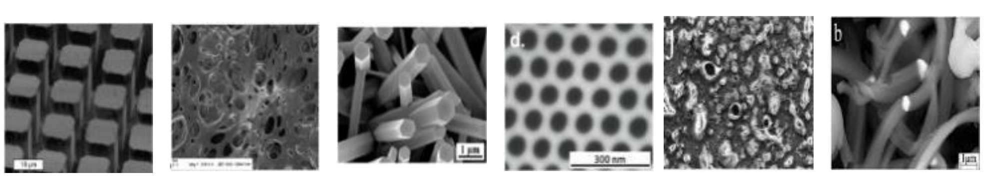
Immersion: simple but difficult to fill fine pores.
Solvent replacement: complicated; good for fine pores.
Vacuum: efficient; good for fine pores.

Oil selection

Chemically inert, low volatility
Surface energy: if too low, cloaking; if too high, low liquid repellency
Viscosity: if too low, not durable; if too high, hard to flow
Fluoroether, mineral oil, tung oil, silicone oil, linseed oil, wax, ionic liquids

Substrate fabrication

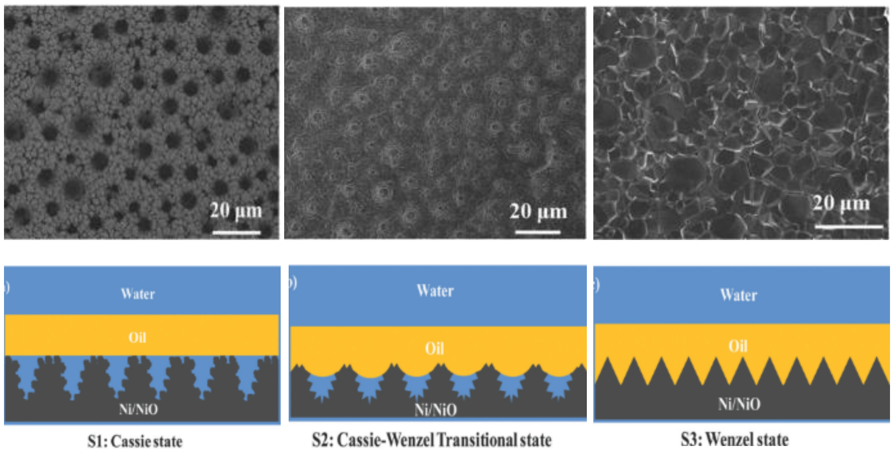
Substrate type: porous, textured, nanowires
Fabrication method: etching, sol-gel, anodization
Pore size: not too big, not too small



Surface modification

Soaking in solutions containing low surface energy materials for surface grafting

Fabrication principle



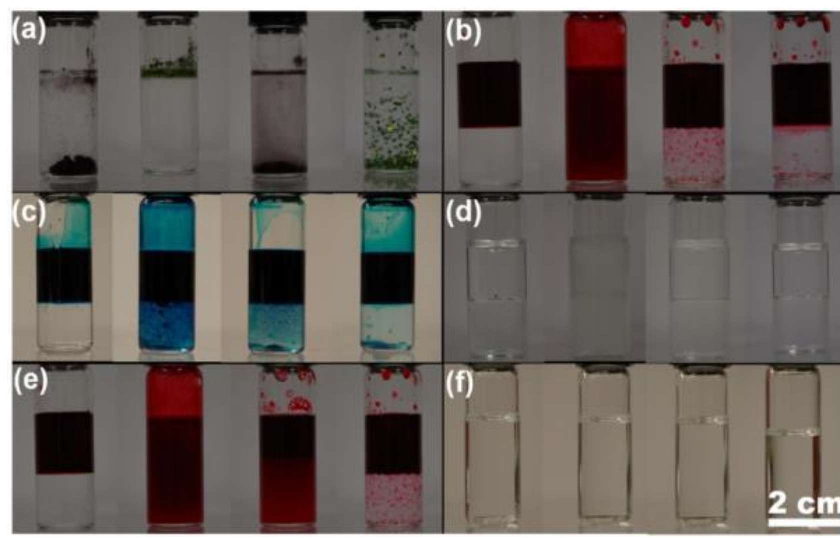
Surface roughness

Surface with nanoscale roughness is better at retaining the oil in SLIPS/LIS.

For superhydrophobic surfaces, hierarchy of micro/nanostructures are better.

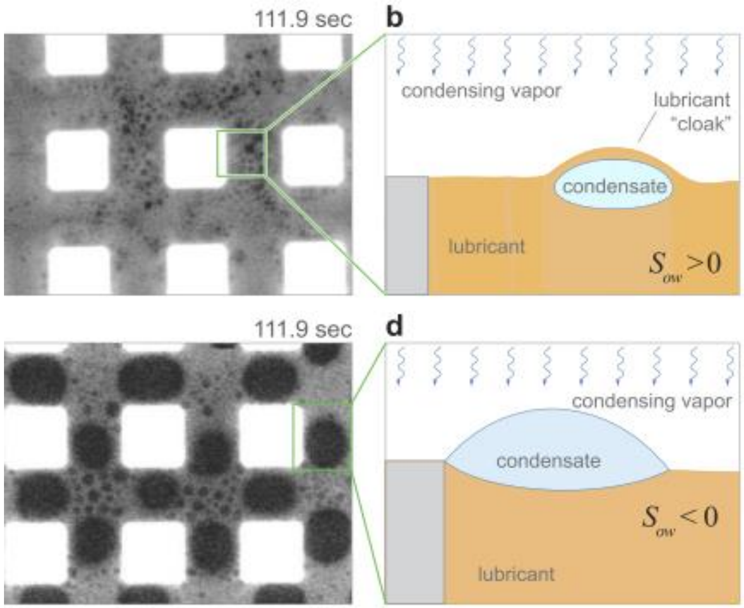
Chemical stability of oil

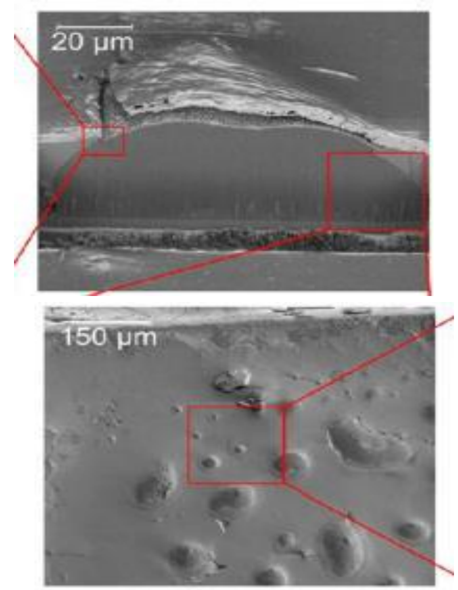
Perfluoropolyether presents the best chemical inertness, however, the extremely low surface energy facilitates cloaking of water. Mineral oils and ionic liquids do not cloak water. Silicone oils have the highest immiscibility with other liquids.



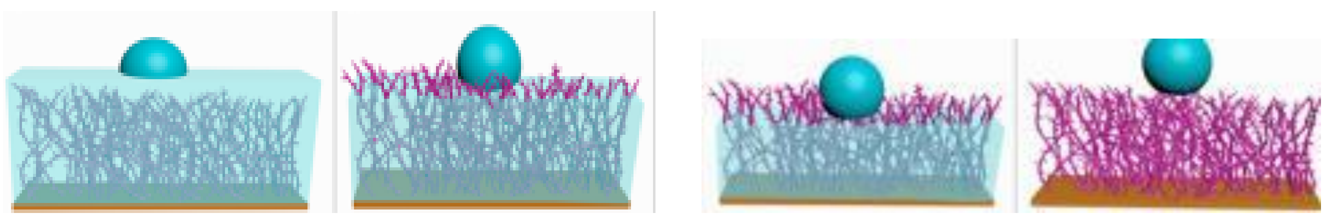
Challenges for LIS/SLIPS

Cloaking – loss of oils; water penetration to the substrate





Environmental attack – immersion; mechanical; temperature; UV



How to prolong the service life of LIS/SLIPS?

Durable lubricant infused AAO surfaces with high-aspect-ratio nanochannels

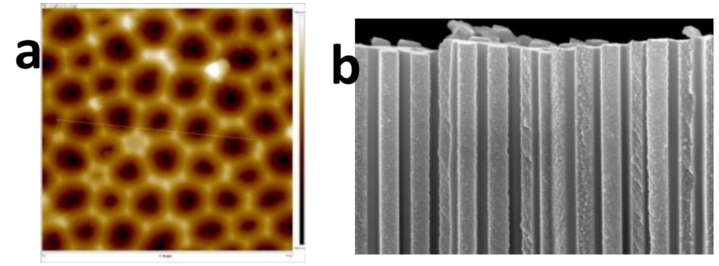
1. Lubricant in deep AAO pores

Highly ordered and high-aspect-ratio cylindrical AAO provide perfect containers for lubrication.

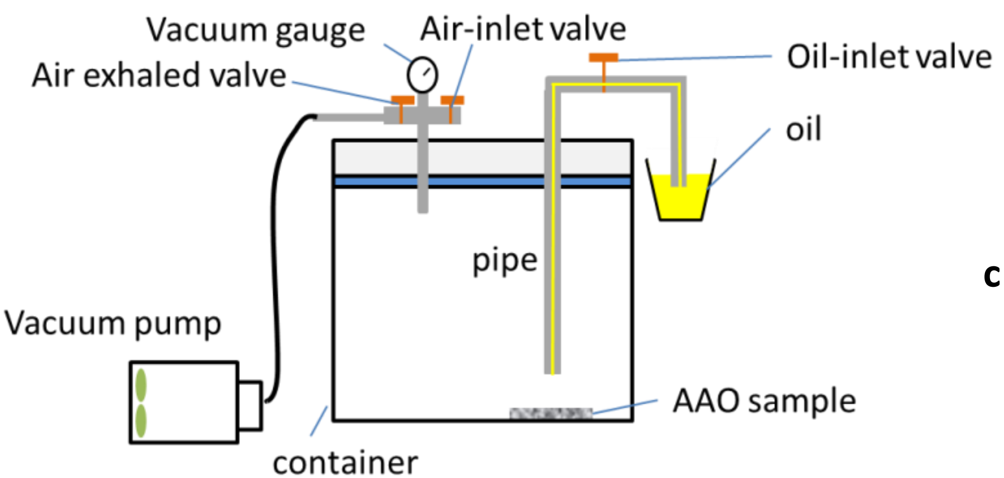
AAO film with pore diameter of 160-200 nm and pore depth of **50 um**.

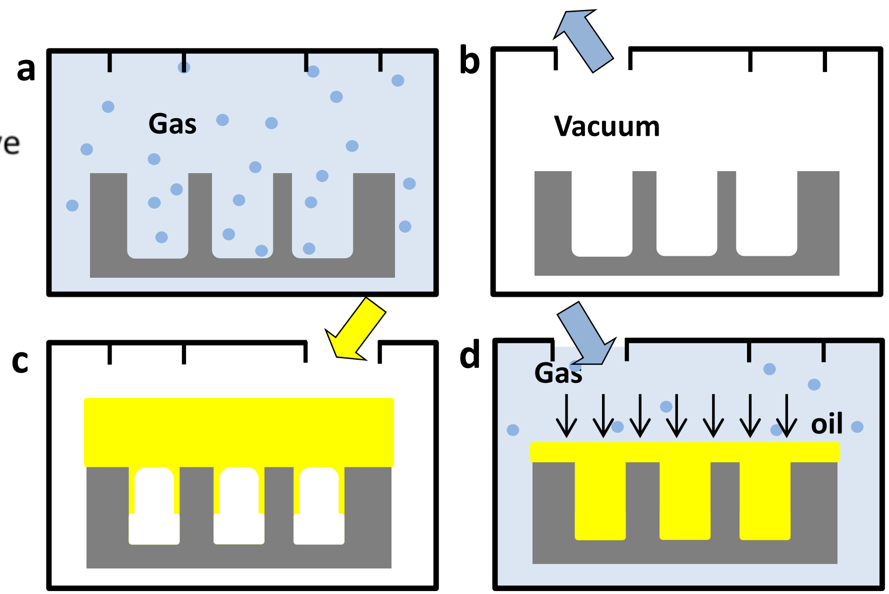
✓ **Thick oxide**
✓ **More oil**

→ **Durability**



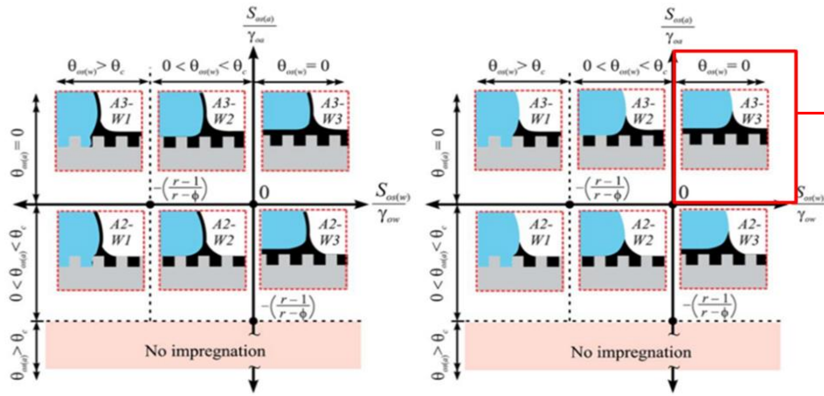
Vacuum impregnation method, to infuse the lubricant into the **high-aspect-ratio** nanochannels





1. Design criteria

The design of LIS based on the understanding of interface between lubricant, substrate, air, liquid droplets. The stable LIS/SLIPS surface should meet strict criteria:



Only this one is a stable surface

- ✓ The oil should spread on the substrate:

  $S_{os(v)} = \gamma_{sv} - \gamma_{os} - \gamma_{ov} > 0; \ \theta_{os} = 0$

- ✓ The droplet should not be cloaked by the lubricant:

  $S_{ow(v)} = \gamma_{wv} - \gamma_{ow} - \gamma_{ov} < 0; \theta_{ow(v)} > 0$

- ✓ The droplet should not completely spread on lubricant

  $S_{wo(v)} = \gamma_{ov} - \gamma_{wo} - \gamma_{wv} < 0; \theta_{wo(v)} > 0$

- ✓ The lubricant is immiscible with external liquid

  $\gamma_{ow} > 0$

Oil on Al2O3

0

Water on Al2O3

62

Water on oil

99.4

Stored for 85 day

1. Cryo-SEM morphology

full impregnation

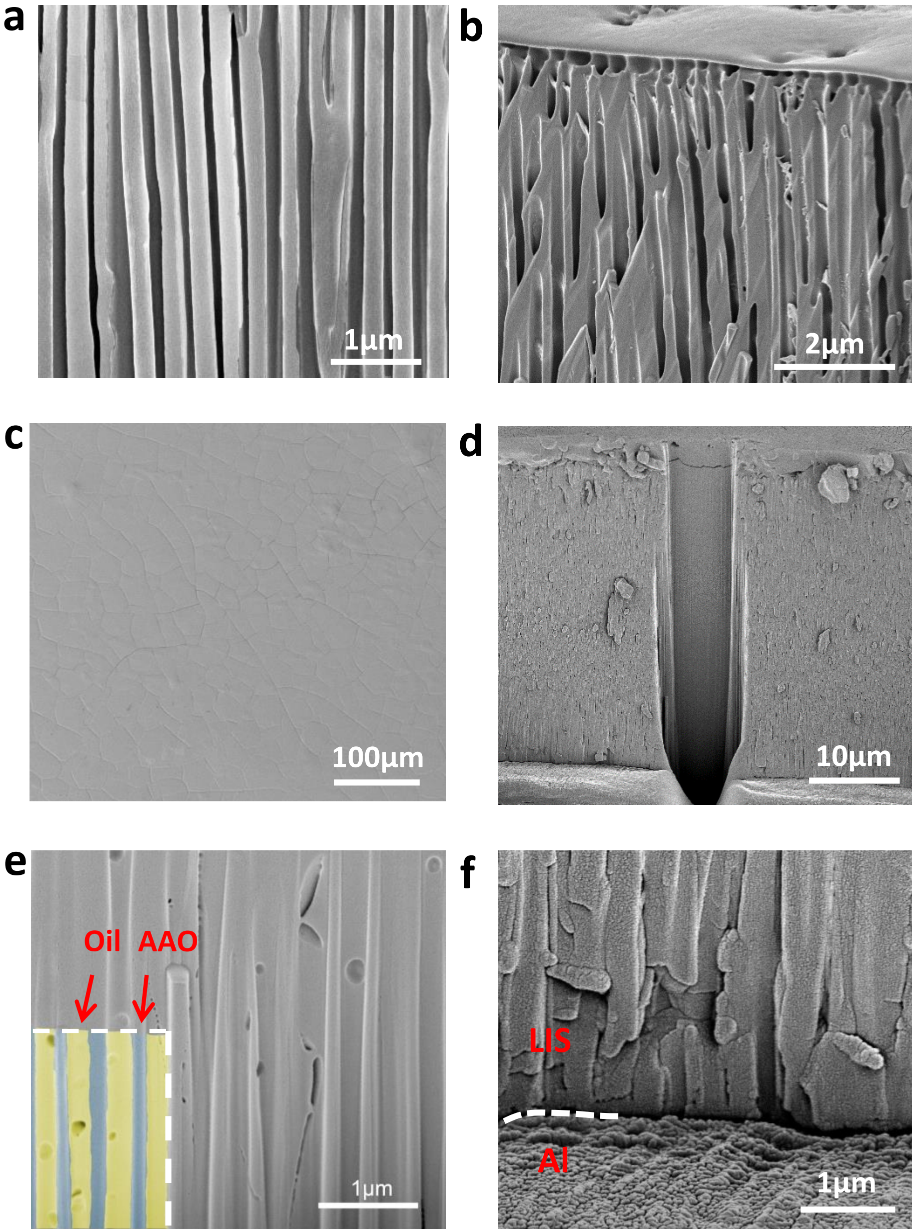


Table The quantity and depth of infused lubricant by vacuum immersion and atmosphere immersion

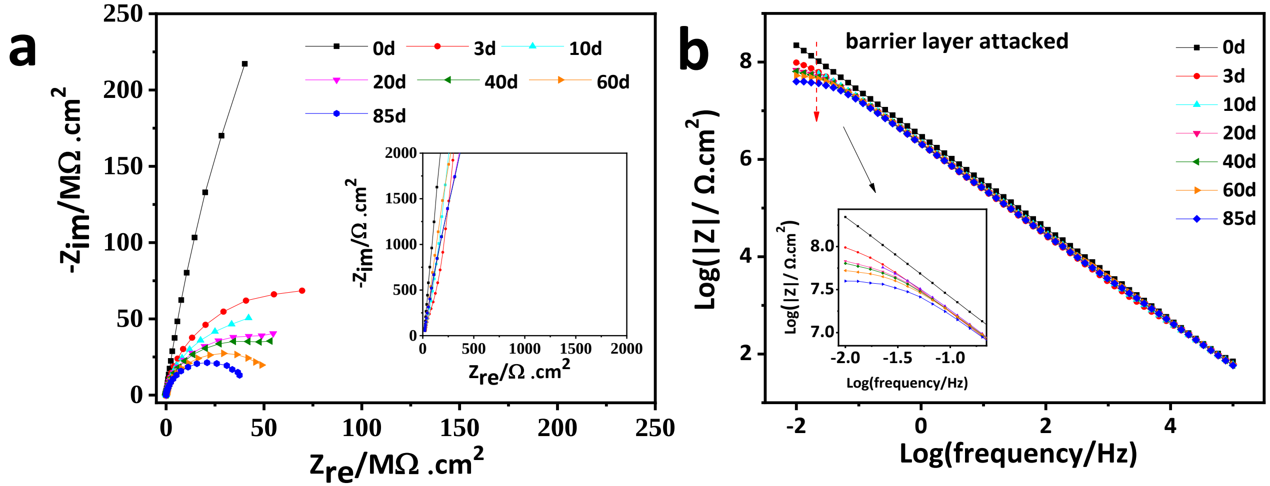
sample	Initial mass (M_0/mg)	Mass after infused (M_1/mg)	Oil mass (M_L/mg)	Depth of infiltration (t/μm)
1	617.74	618.86	1.12	5.89
2	618.32	619.40	1.08	5.67
3	632.30	633.32	1.02	5.86
Superficial impregnation				
4	608.93	617.96	9.03	47.48
5	624.92	634.31	9.39	49.37
6	647.80	656.91	9.11	47.90
Complete impregnation				

Figure Cryo-SEM images of the cross sections of (a) empty nanochannels of AAO and (b) pores of AAO after simple immersion; (c) top view of LIS; (d) full cross section of FIB-milled LIS fabricated by vacuum impregnation; (e) magnification of the oil infused nanochannels; (f) magnification of the boundary between the oil infused nanochannels and the aluminum substrate.

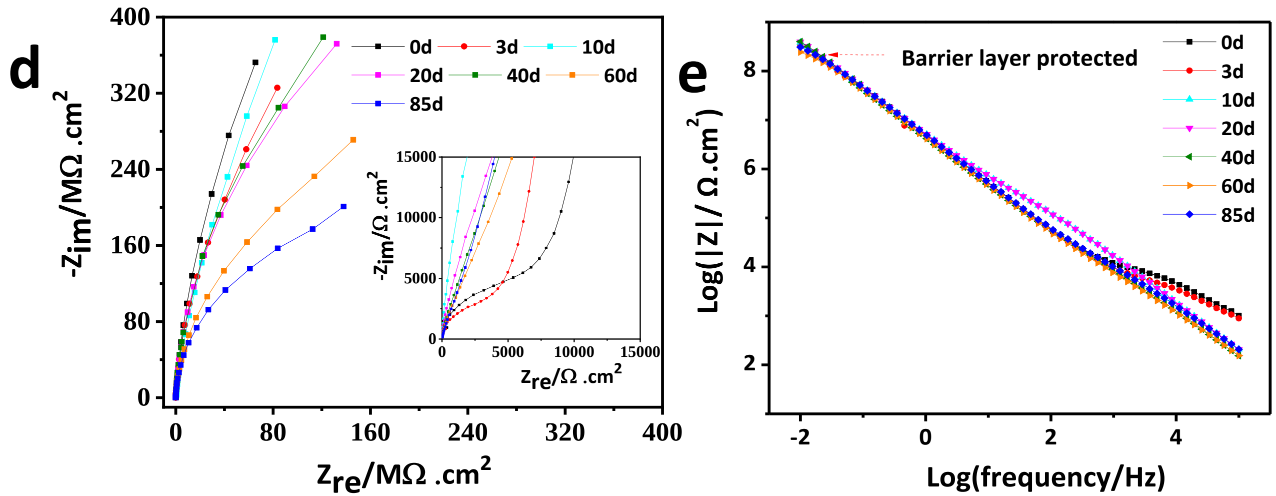
1. EIS analysis

corrosion protective property

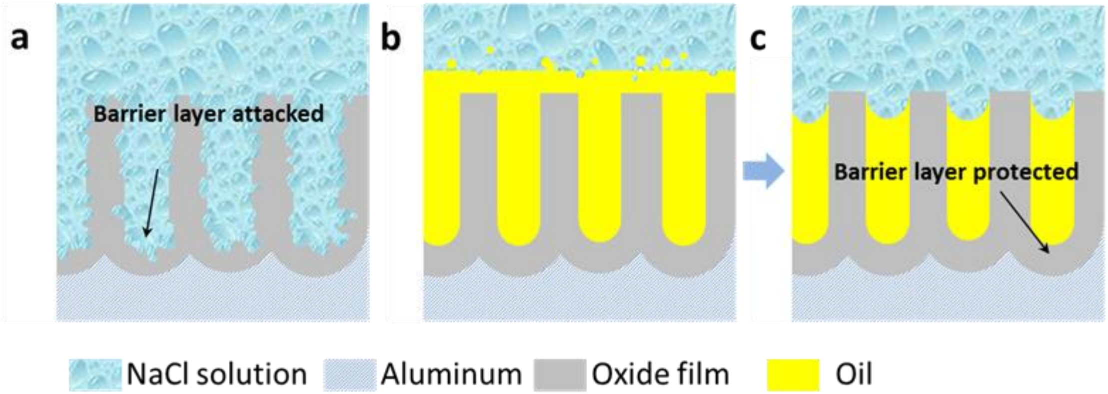
- For bare AAO: Value of $|Z|_{0.01Hz}$ progressively decreased which was caused by attack of water/electrolyte penetration.



- For LIS, the low frequency regions over-lapped indicating a stronger protective performance. High frequency region slightly decreased, reflecting the gradual loss of the surface-adhered lubricant layer under immersion environment



1. Long-term protection performance



Scheme (a) barrier layer of AAO attacked by penetrated corrosive solution;(b) dissolution of the oil layer adhered to LIS and (c) barrier layer protected by the remaining oil in the nanochannels

- After immersion for 85 days, only 3 µm of the infused lubricant was lost . The remaining most of the lubricant was well trapped in the nanopores to resist further solution penetration.

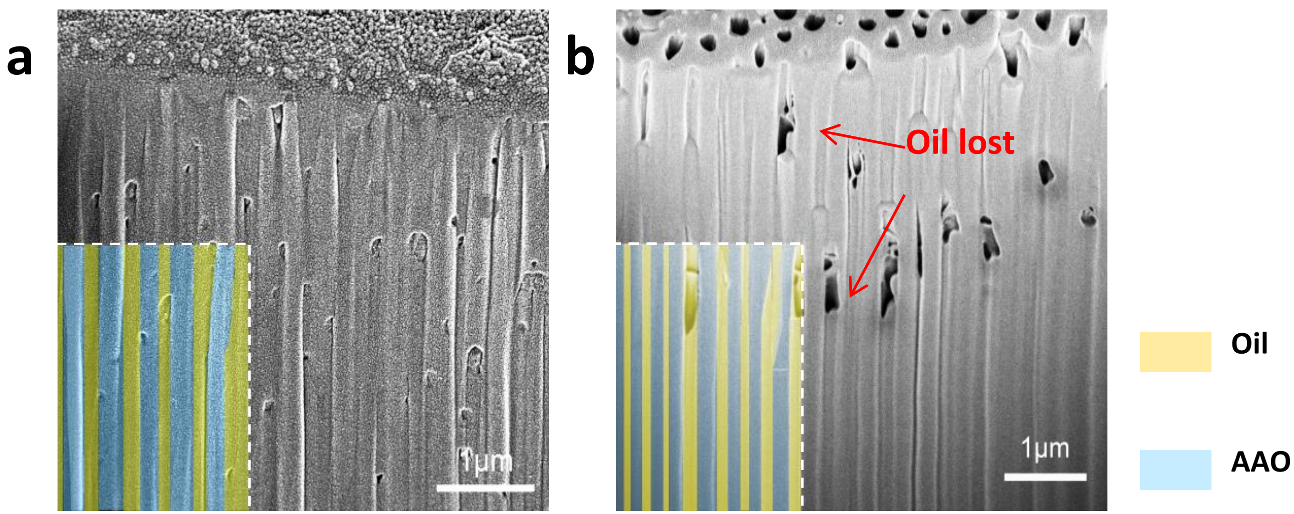
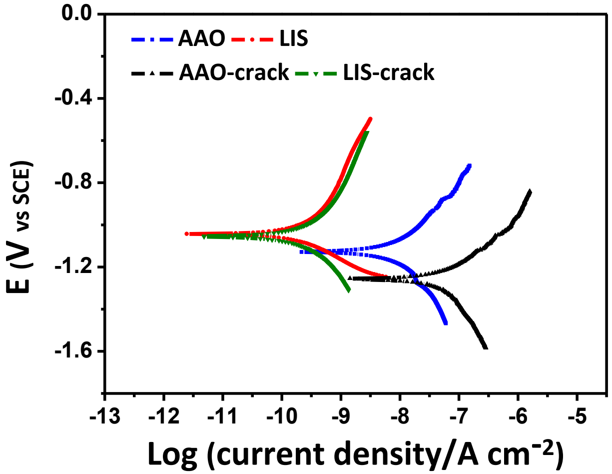


Figure Cryo-SEM image of LIS in different immersion stages: (a) upper lubricant layer dissolved after 10 days (b) ~3 µm thick lubricant lost in the nanochannels after 85 days.

1. Self-healing mechanism



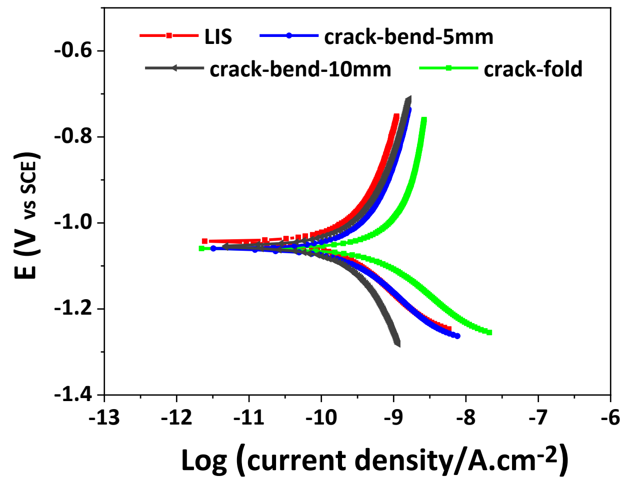
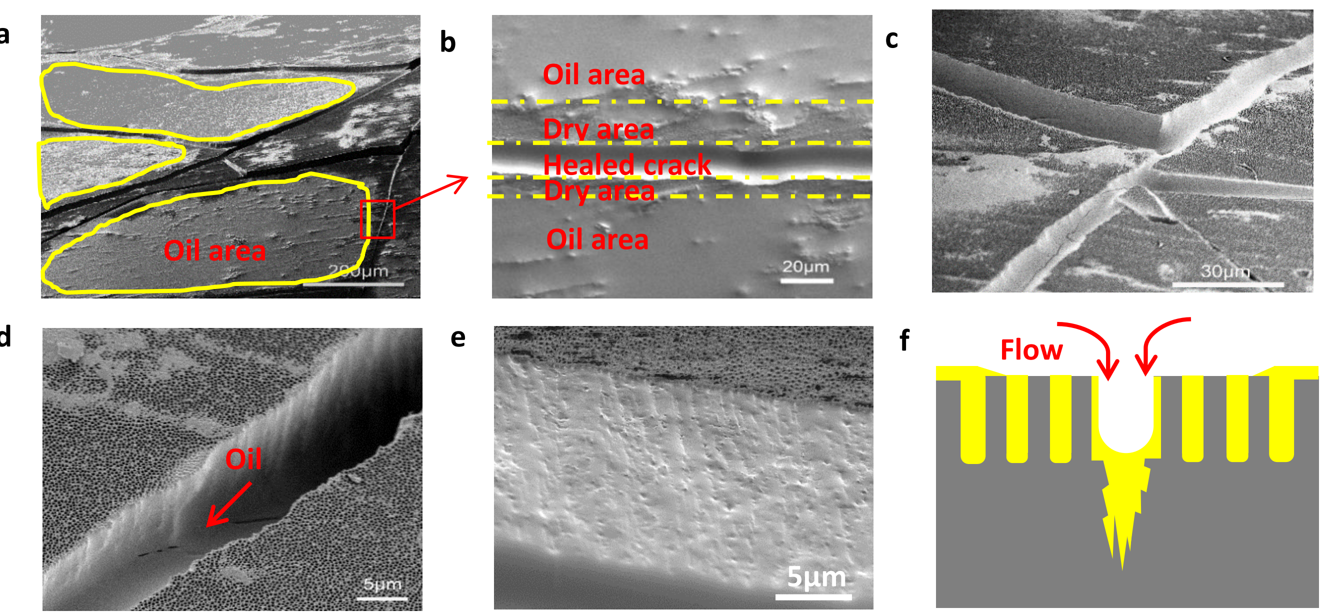


Figure Potentiodynamic polarization results for the intact and damaged samples (bare AAO and LIS), (b) thick LIS cracked under different conditions

- the corrosion potential of the cracked LIS remained almost the same as that of the intact LIS and the corrosion current density was only slightly higher
- the polarization curves of the LIS bended around 5 mm diameter cylinder rod almost overlapped with that of the intact LIS. The corrosion current density of the folded LIS was only slightly higher, indicating the excellent self-healing property



- the in-flow of lubricant from the nanochannels in the surrounding intact surface cover the exposed surface

1. Mechanical durability

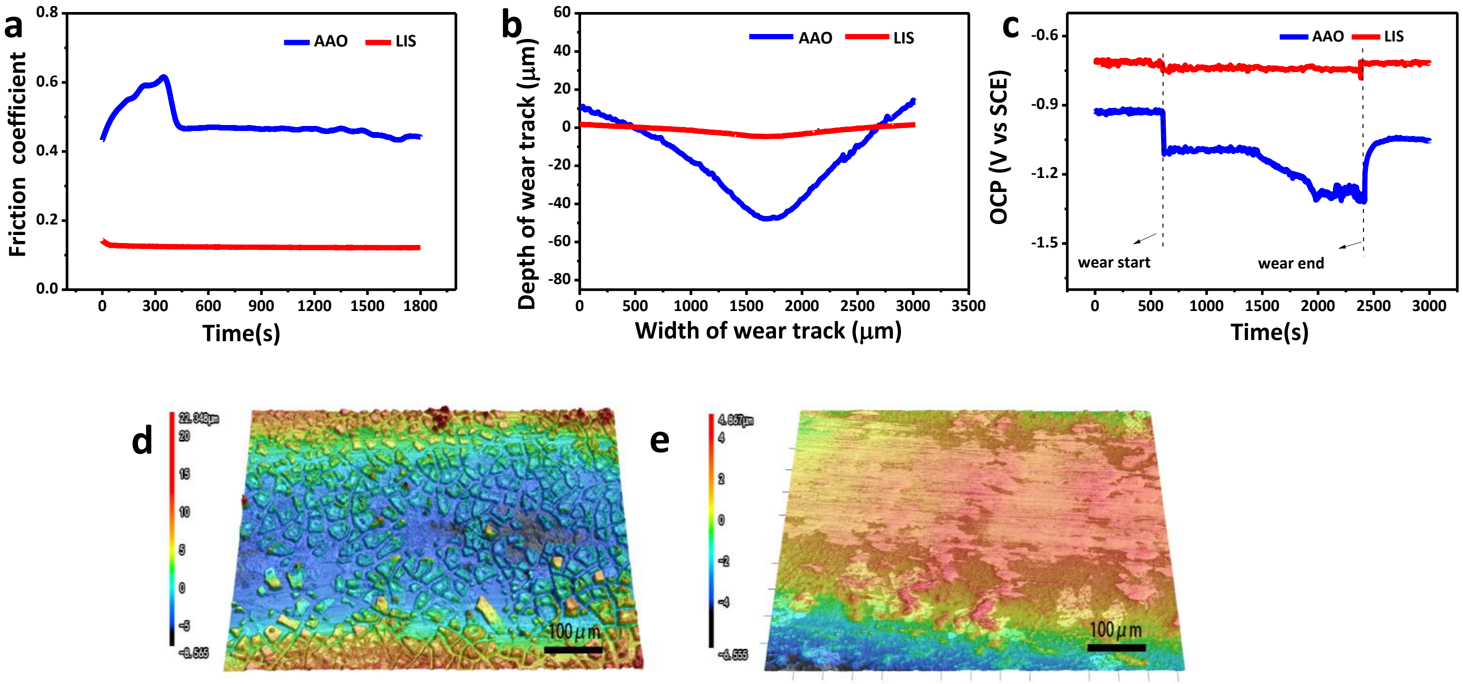


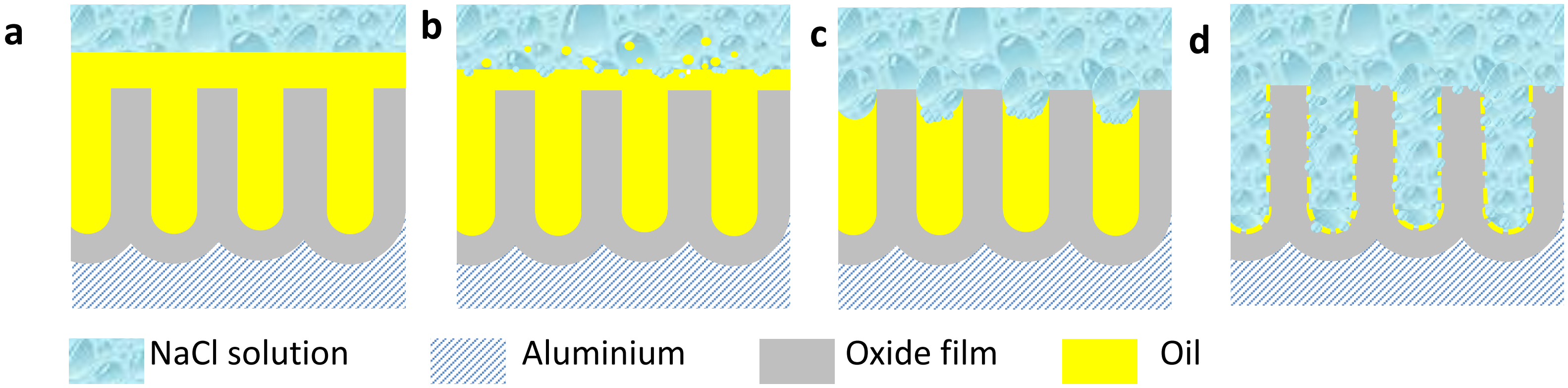
Figure Tribological behavior of bare AAO and LIS: (a) friction coefficient during sliding, (b) depth of wear track and (c) open circuit potential during sliding; CLSM image of (d) worn bare AAO and (e) worn LIS after wearing for 1800s

- The anodized film of the bare AAO was crushed into small pieces, while the LIS specimen remained relatively intact because of its low CoF and the self-healing action.
- much higher OCP values of the LIS are observed than that of the bare AAO during the entire testing period

Deterioration of lubricant-infused AAO surface during long-term exposure in NaCl solution

2. Deterioration study

Because of the **high mobility of the liquid lubricant**, the stability of LIS/SLIPS as a protective or functional surface **during long-term environmental exposure** is questionable.



Challenge of the deterioration study of LIS/SLIPS

- The long-term stability and degradation of the LIS/SLIPS in the proposed service environment has rarely been studied.
- The quantity of the lost lubricant is difficult to analyse.
- The transition points of lubricant lost in different stages are difficult to identify.

2. Cryo-SEM morphology

top oil layer dissolution

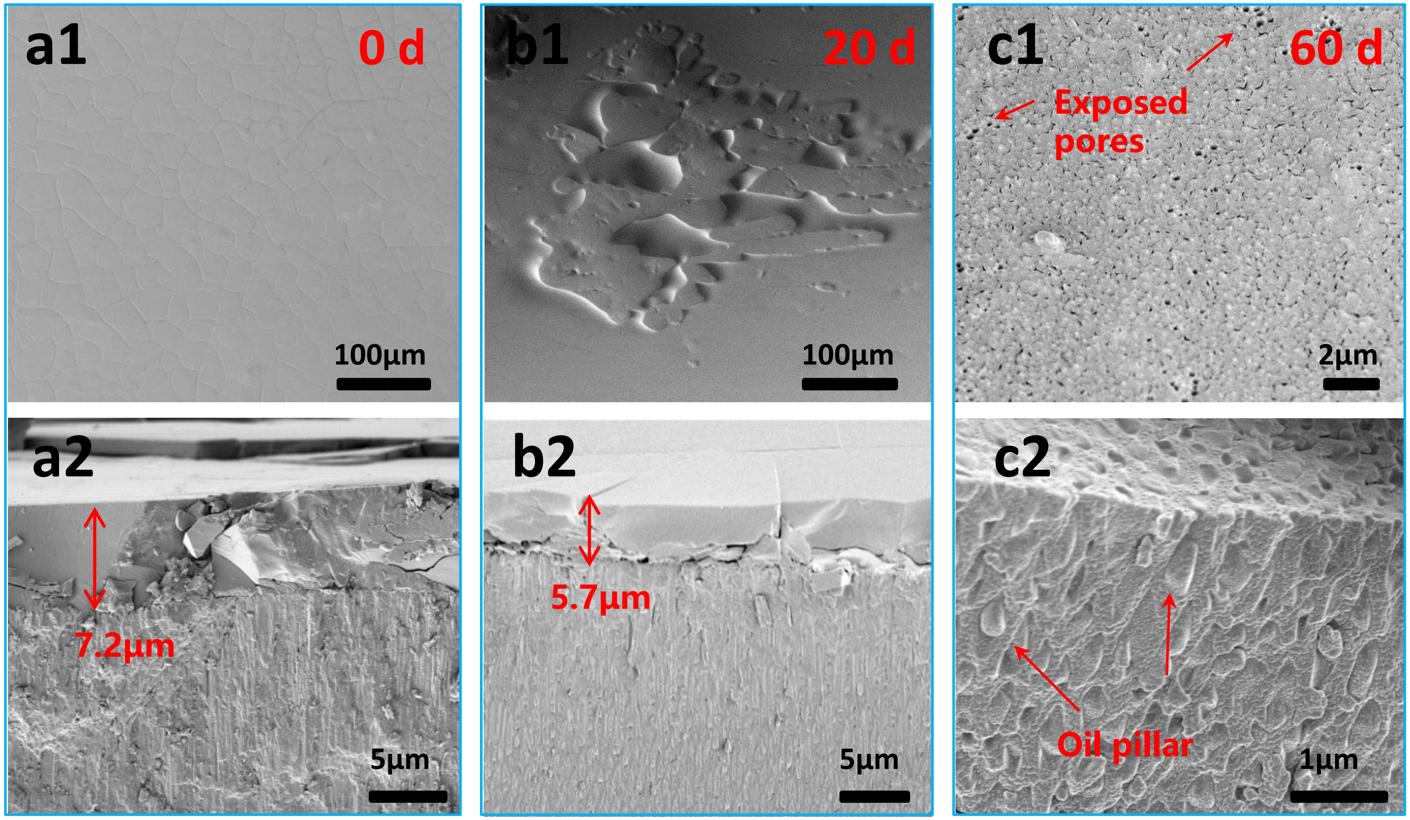


Figure Cryo-SEM images showing (1) top view and (2) cross section of LIS during immersion in 1 M NaCl solution for (a) 0, (b) 20, and (c) 60 days.

- a continuous and smooth lubricant layer can be observed initially, but finally nanoporous surface was exposed and some pores became visible.

2. Cryo-SEM morphology pore-infused oil dissolved

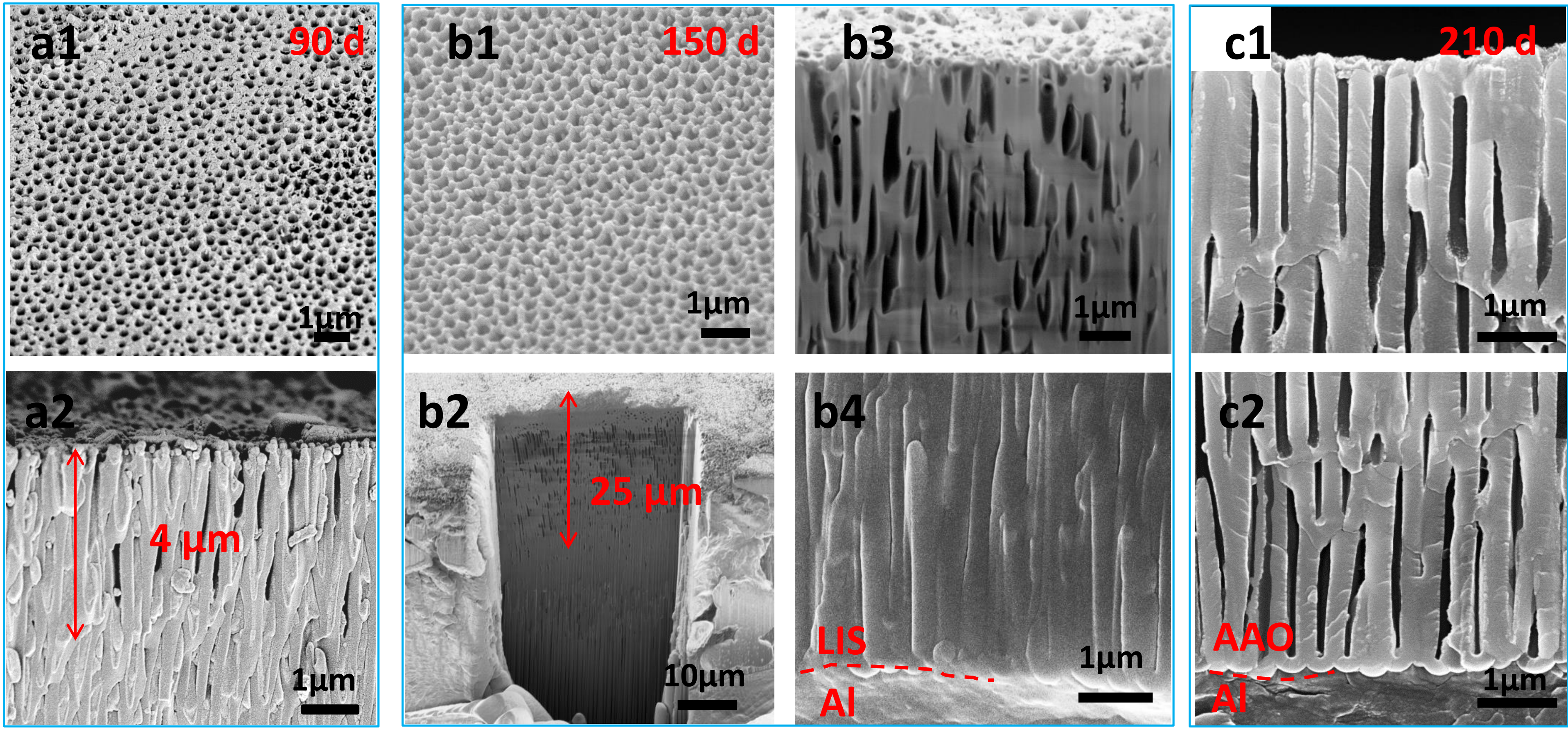


Figure Cryo-SEM image of LIS during immersion in 1 M NaCl solution for (a) 90, (b) 150 and (c) 210 days. (a1) Top view, (a2) upper cross section. (b1) Top view, (b2) entire cross section, (b3) upper cross section, and (b4) bottom cross section. (c1) Upper cross section, (c2) bottom cross section.

- the lubricant further depleted from the nanochannels gradually.

2. Surface wettability

from sliding to pinning

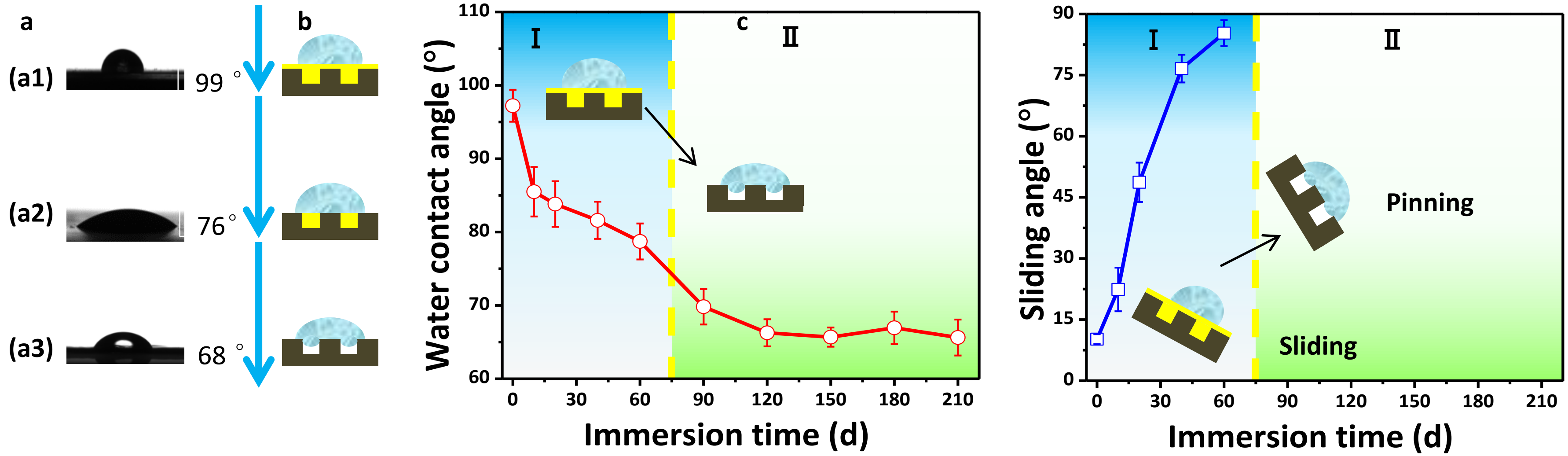
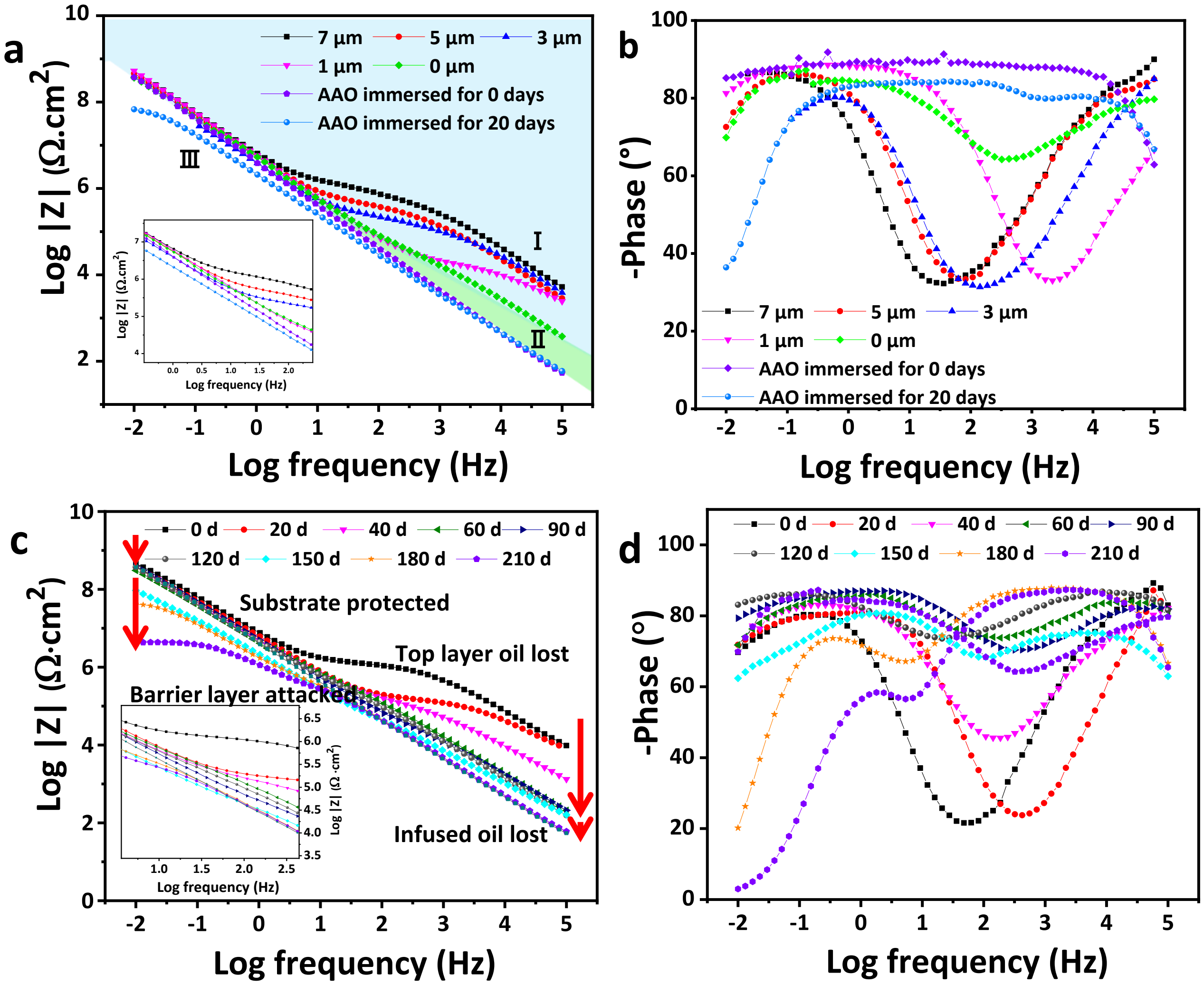


Figure (a) WCA on (a1) surface covered by oil layer, (a2) solid and oil composite surface, and (a3) solid and air composite surface. (b) WCA and (c) SA of LIS during different deterioration stages.

- From the 60th day to the 90th day of immersion, the WCA decreased from 78° to 69°, which was attributed to the **exposure of the AAO porous substrate.**
- The droplet transited from sliding to pinning indicated the **exhaustion of the top lubricant** layer and the exposure of the porous AAO substrate.

2. EIS measurement

long-term immersion



- The deterioration of LIS could be **divided into three stages**: (Ⅰ) the dissolution of the surface-adhered lubricant, (Ⅱ) the diffusion of the infused lubricant and (Ⅲ) the corrosion attack of the barrier layer.

- The |Z| in **high-frequency region** declined as the thickness of the surface oil layer decreased. |Z| in the **low frequencies** decreased indicating corrosion of the barrier layer

Figure (a) Impedance modulus plots and (b) phase angle plots for LIS with controlled top layer lubricant thicknesses, bare AAO immersed in 1 M NaCl solution for 0 and 20 days. (c) Impedance modulus plots and (d) phase angle plots of LIS during immersion in 1 M NaCl solution for up to 210 days.

Durable deicing LIS based on a photothermal responsive lubricant

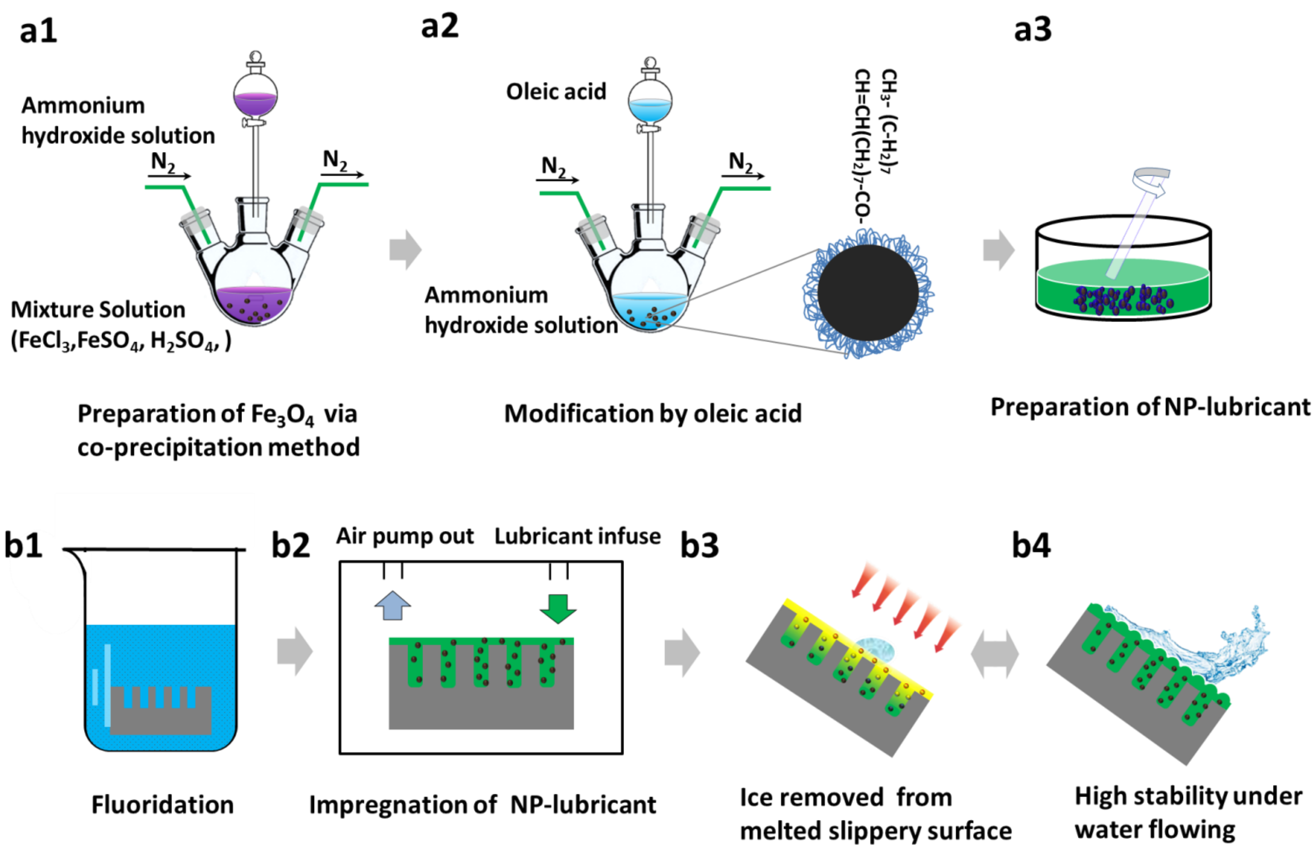
3. Background

fabrication of responsive LIS

Surface with Smart response to environment

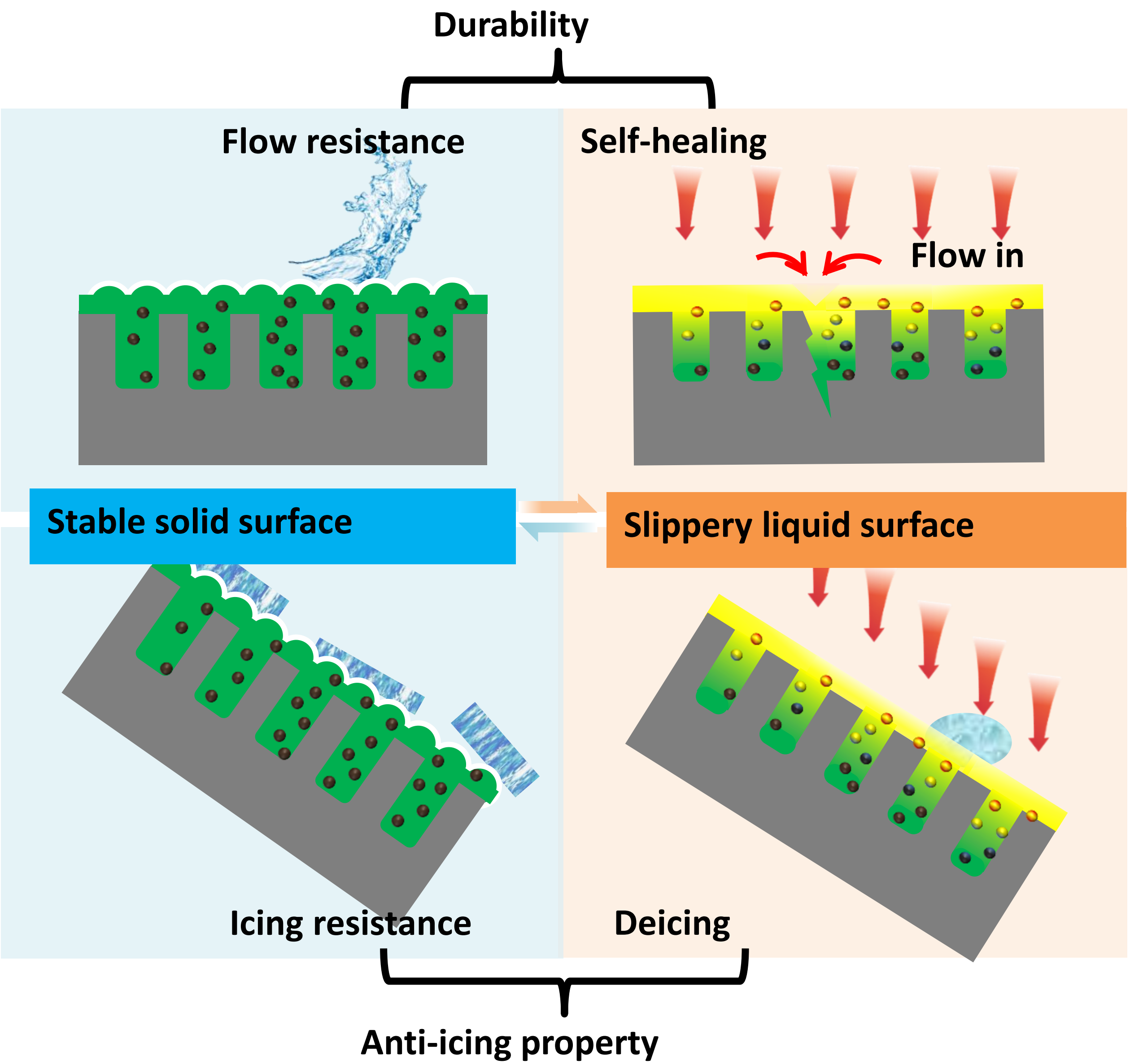
Static → Dynamic

Passive protection → Smart response



Scheme (a) Preparation scheme of photothermal responsive lubricant. Schematic illustration of the fabrication process and application of the photothermal responsive lubricant infused surface

3. Photothermal responsive LIS



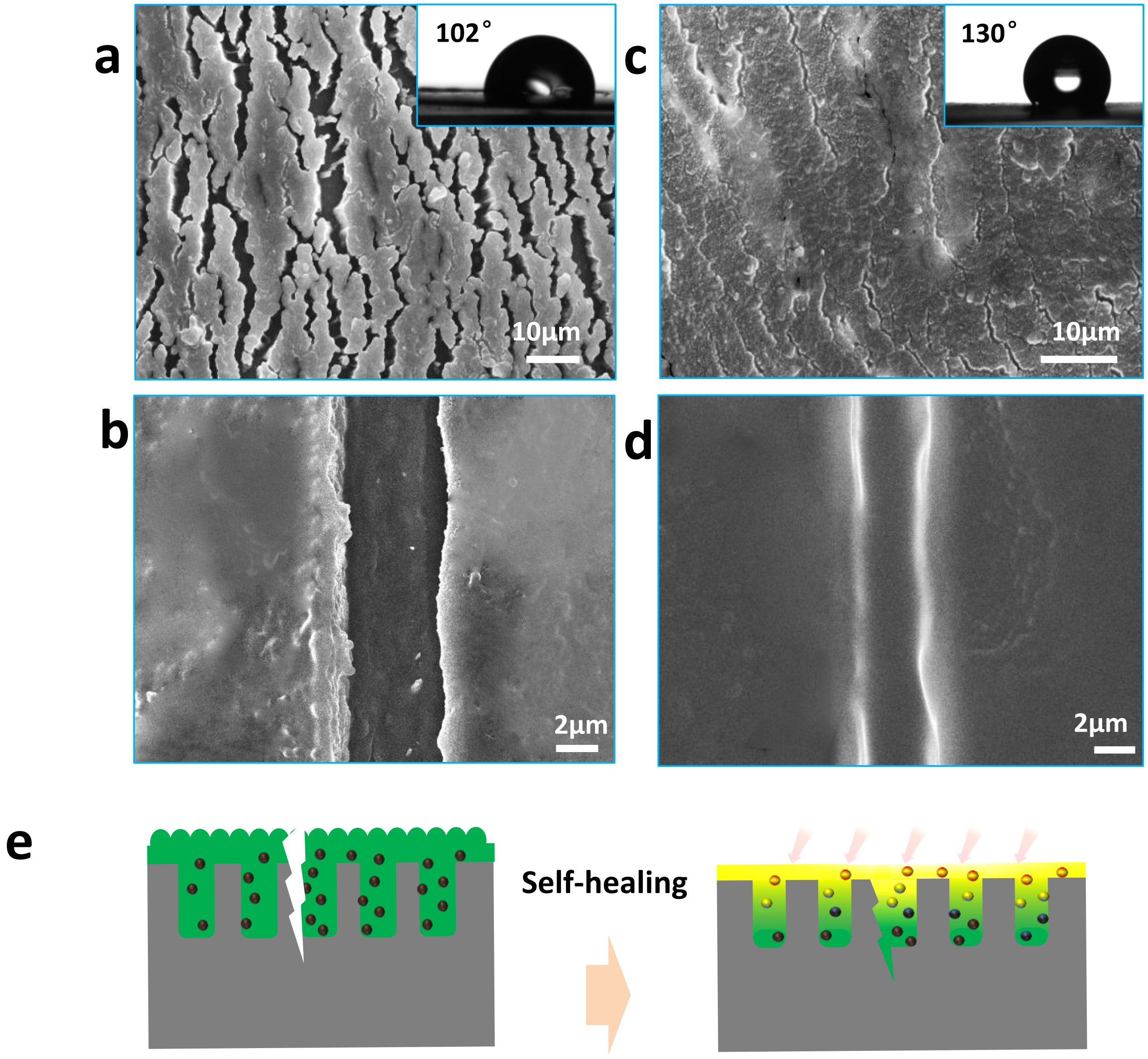
✓ **photothermal responsive lubricant**

☐ Solid state :
stable, low surface energy
protect the substrate; antiicing

☐ Liquid state:
Movability, low surface energy
Self healing, deicing,

3. Self healing

cracks repaired



- After IR irradiation, most of the cracks were healed, the rough surface became smooth and the surface hydrophobicity recovered.

Figure (a) Cracks and exposed substrate on the NP-LIS; (b) Magnification of (a); (c) cracks were healed and recovered (d) magnification of (c)

Summary

Fabrication of durable LIS with high aspect ratio nanochannel

- A complete impregnation of lubricant into ultra high aspect ratio nanopores is effectively achieved by vacuum immersion.
- Cryo-SEM gives an insight to the self-healing mechanism
- Long term anticorrosion property and mechanical durability of LIS may be attributed to the dual protection of the thick oxide substrate and the lubricant.

Deterioration of LIS during long-term immersion

- The deterioration included lubricant dissolution from the surface and then the pores of AAO.
- Cryo-SEM observation and quantitative analyses by UV spectroscopy and EIS were employed to describe the dissolution of lubricant.
- AAO defects could accelerate lubricant dissolution and corrosion attacks.

Durable deicing LIS with switchable hydrophobicity/slipperiness

- The dual actions of surface heating by irradiation and slipperiness of melted lubricant promoted frost thaw and significantly reduce the ice adhesive strength.
- Combination of the self-healing effect of melted lubricant and robustness of solid lubricant imparted enhanced durability to the surface.

Bedankt voor uw aandacht!

smeermiddel-geïmpregneerd geanodiseerd aluminium

Arjan Mol

Dequan Wu, Lingwei Ma, Dawei Zhang, Badar Minhas, Bei Liu, Hongchang Qian, Herman Terryn, Xiaogang Li

Vereniging Industrieel Oppervlaktebehandelend Nederland