Multilayer Coating with a Superhydrophobic Porous Top Layer for Carbon Steel Corrosion Protection

NATIONAL ENERGY TECHNOLOGY LABORATORY

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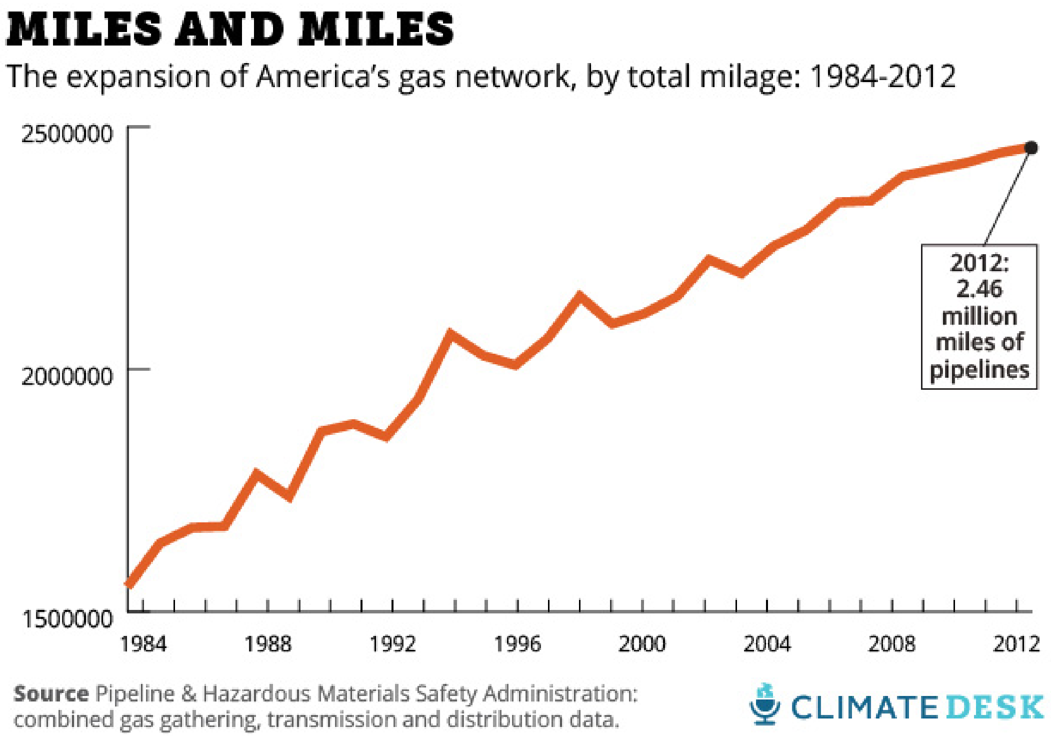
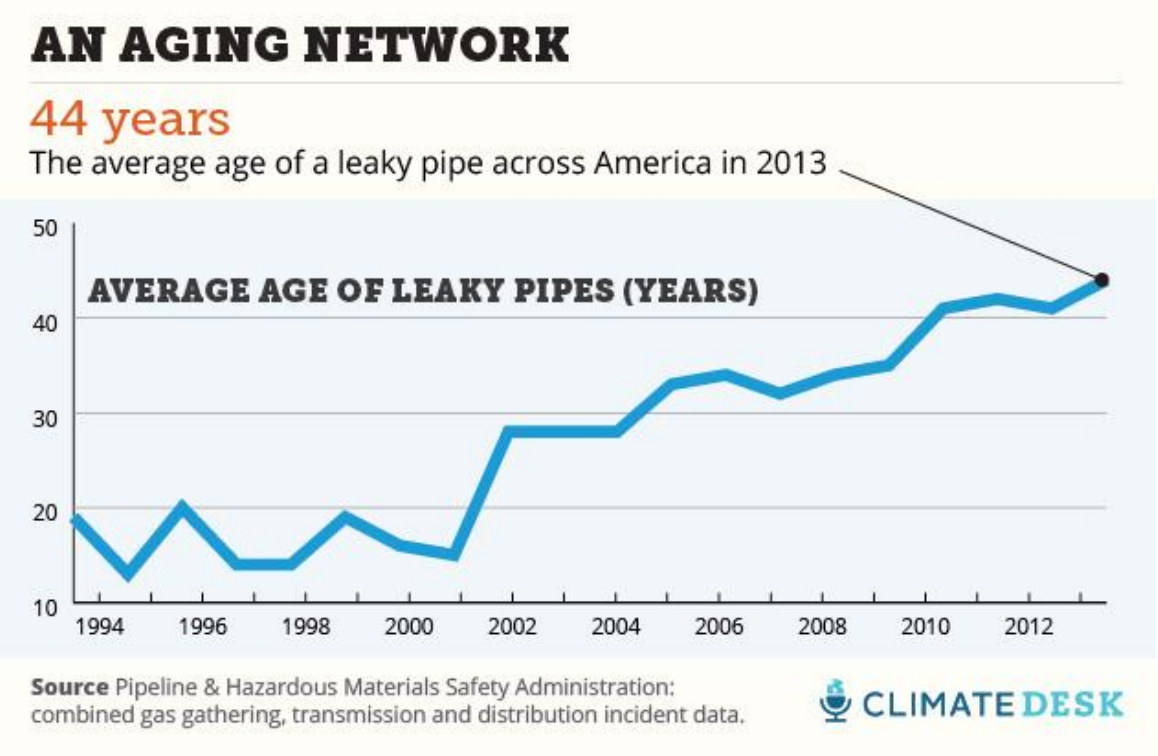
A Vast and Aging Natural Gas Pipeline Network

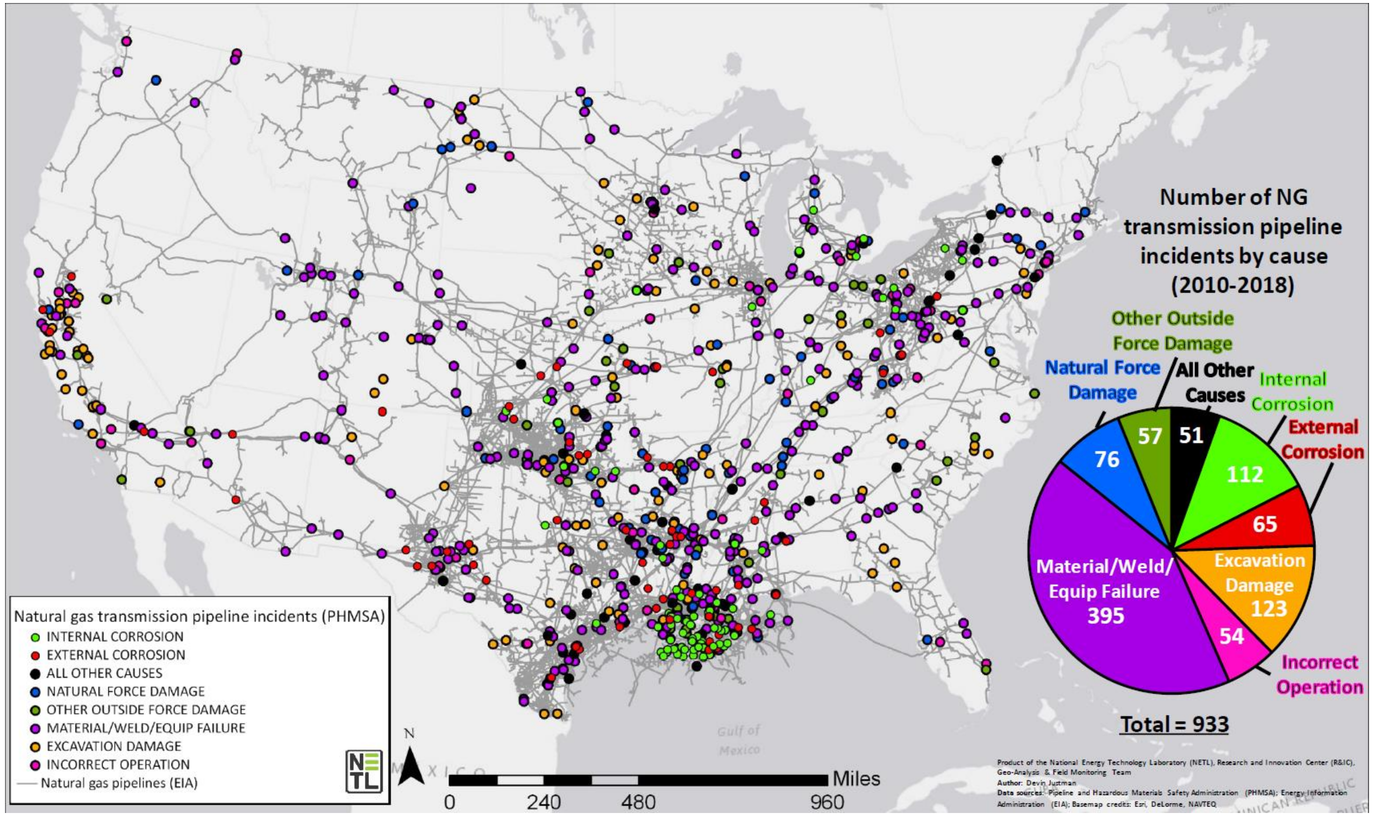




Natural Gas Leaks are Common

There are more leaks caused by internal corrosion than external corrosion.

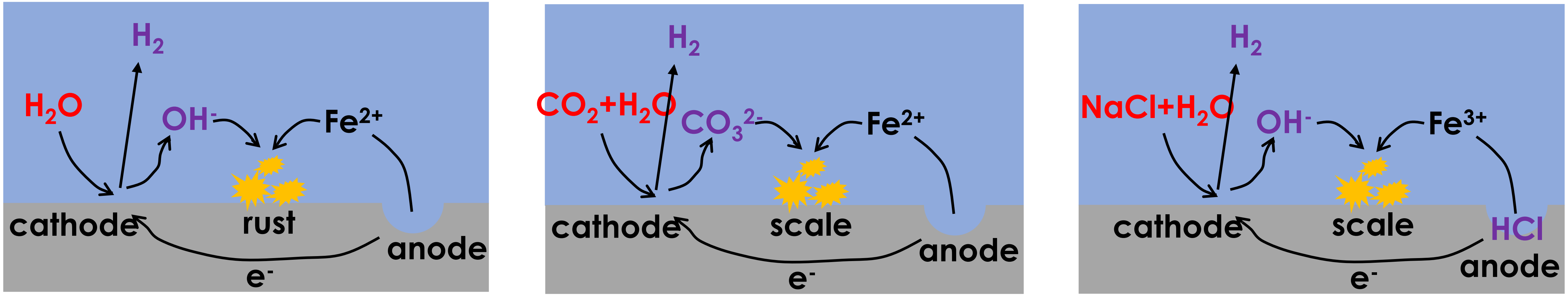
Natural gas leaks can be reduced by preventing the internal corrosion of natural gas pipelines.



Product of the National Energy Technology Laboratory (NETL), Research and Innovation Center (RIC), Geo Analysis & Field Monitoring Team

Corrosive Species in Natural Gas Pipelines

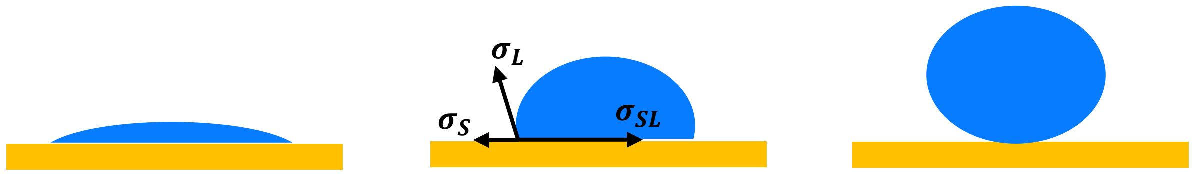
There are three major corrosive species in natural gas pipelines: H_2O, CO_2, and NaCl



To the best of our knowledge, no existing material can handle all three corrosive species at once, e.g.:

- Corrosion inhibitors cannot cover 100% of the surface.
- Metallic coating can be eroded over time.
- Polymer coatings are prone to under-film corrosion.

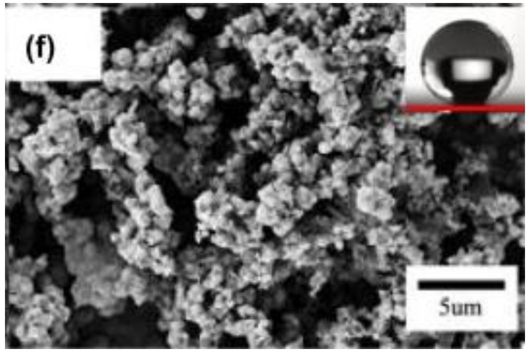
Why Superhydrophobic Surfaces?



hydrophilic θ < 90°   hydrophobic θ > 90°   superhydrophobic θ > 150°

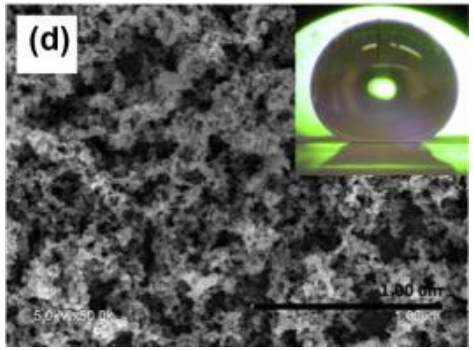
CO_2 and NaCl exist as hydrated ions in an aqueous solution.
Reducing the contact area with the aqueous solution can help reduce corrosion cause by CO_2 and NaCl.

silica-based



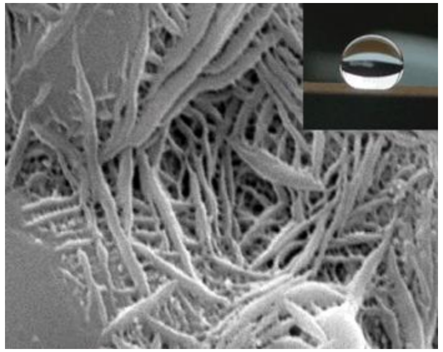
L. Wu, et. al. *Corrosion Science*, 2014, 85, 482-487

titania-based

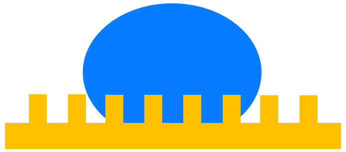


T. T. Isimjan, et. al. *Chemical Engineering Journal*, 2012, 210, 182-187

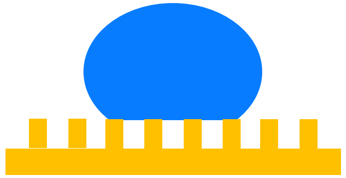
polymer-based



Z. Z. Luo, et. al. *Advanced Materials*, 2008, 20, 970-974



Wenzel model



Cassie-Baxter model

In order to be superhydrophobic, the material needs to be: (1) intrinsically hydrophobic, and (2) porous on its surface and able to trap air in pockets under the liquid.

Superhydrophobic Coating for Corrosion Prevention

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Despite its potential, the anti-corrosion property of hydrophobic coatings was not well quantified in prior studies.

- **Substrates are different**
  Mg, Al, stainless steel, carbon steel
- **Corrosive environment varies**
  acid, base, salt, CO_2
- **Corrosion rate not calculated**
  impedance, corrosion current, corrosion potential were used instead

One comparable study reduced the corrosion rate to 0.45 mm/year in salt water. L. Wu, et. al. *Corrosion Science*, 2014, 85, 482-487

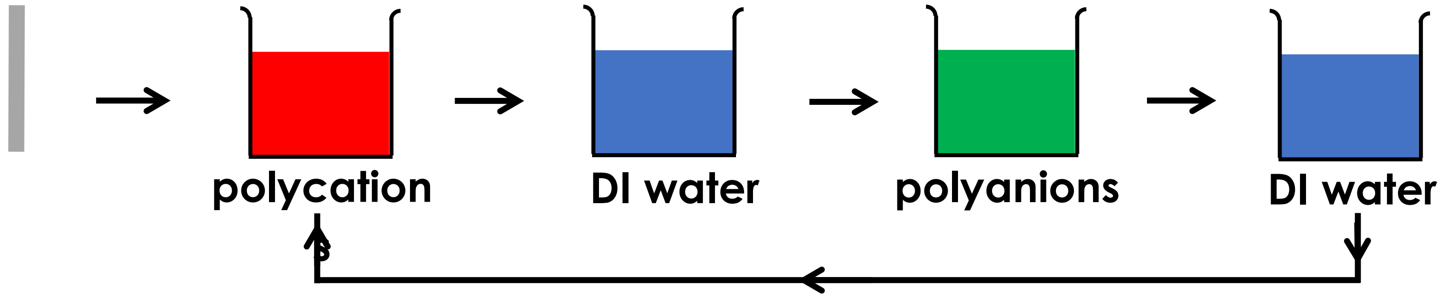
Assuming the wall thickness is 44 mm (a generous assumption), the pipe would be rusted through in less than 10 years under the most severe case.

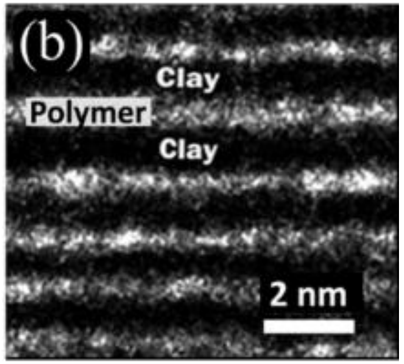
In this study, combine silica nanoparticles were combined with polymers to produce an anti-corrosion coating that can reduce the corrosion rate to < 0.1 mm/year in the presence of CO_2, NaCl, and H_2O. This could extend the service life to ~ 50 years.

Typical Layer-by-Layer (LbL) Assembly

Typically, positively charged components and negatively charged components are alternately deposited one layer at a time.

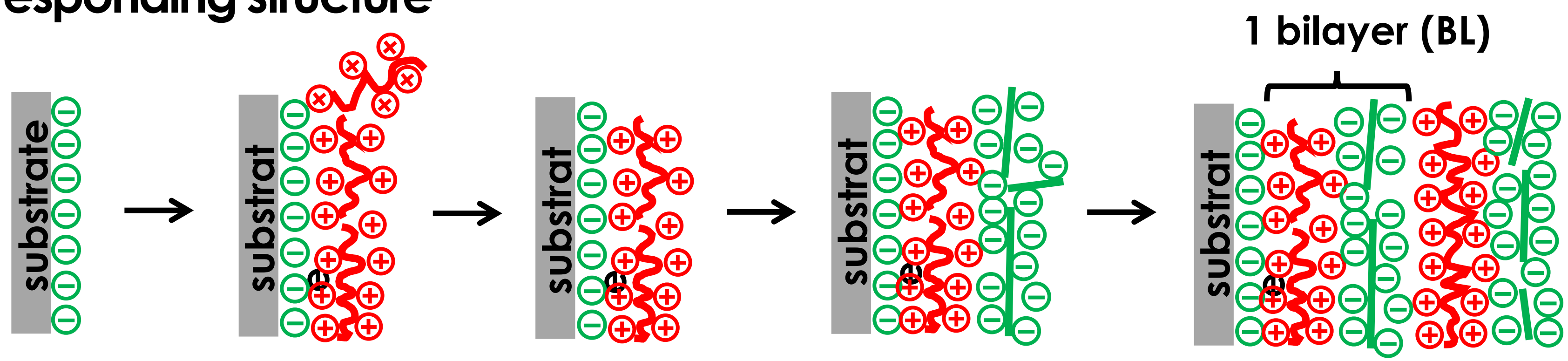
Process





Hagen D. A. *RSC Advances* **2014**, 4, 18354.

Corresponding structure



- **Thin and light**

Reduce material cost

- **Customizable**

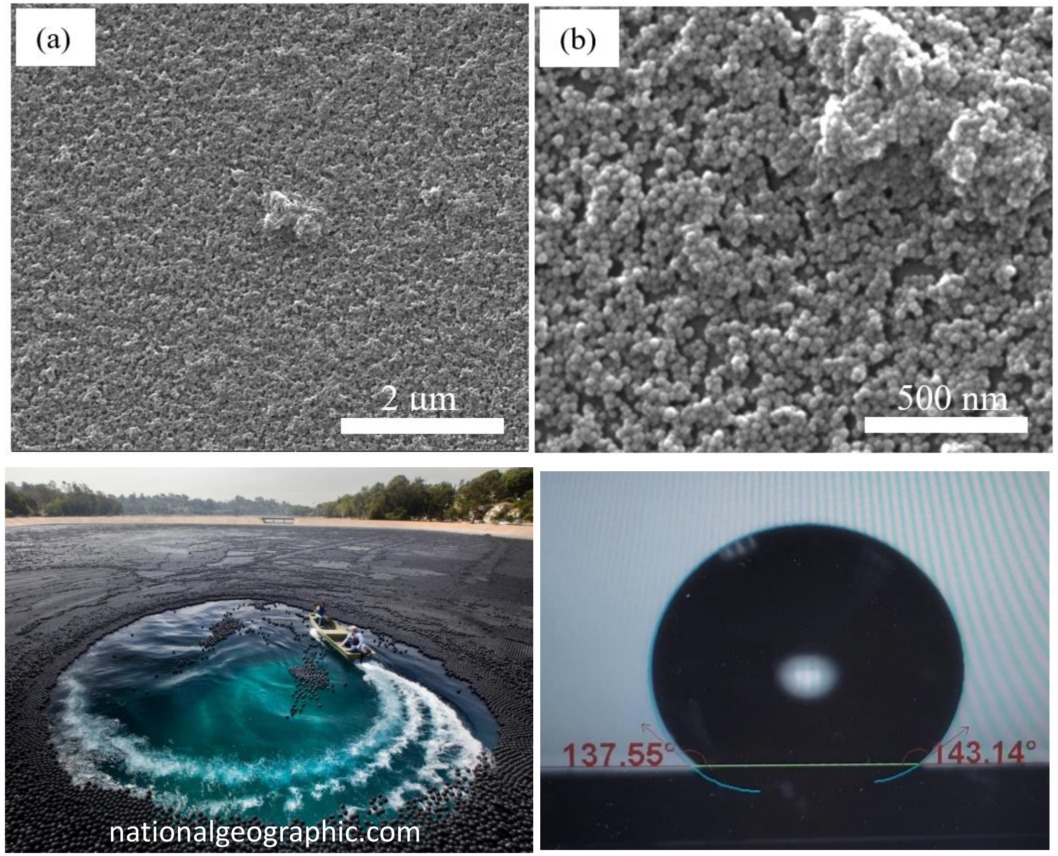
Avoid using toxic component

- **Structural control**

Fine tuning at nanoscale

Polymer/Silica Nanoparticles (SiNPs) Bilayers

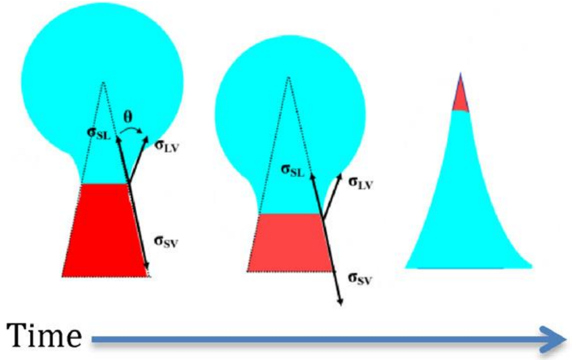
The coating produced using LbL assembly packs SiNPs too well to generate a rough surface. Contact angle <150^{o} after fluorination using (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane.



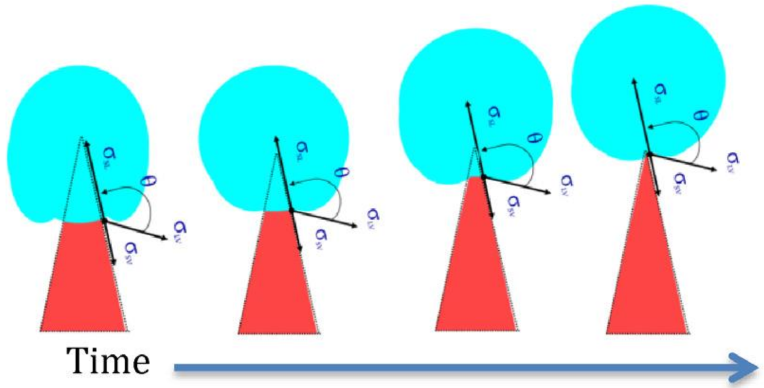
Effective Contact Angle and Surface Roughness

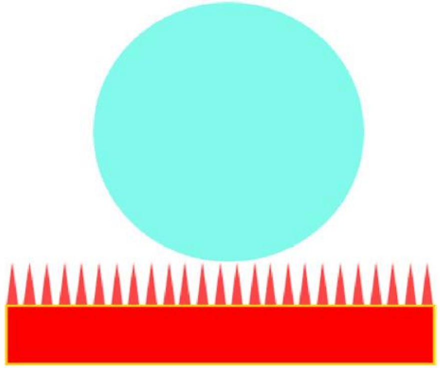
Unlike contact angle, effective contact angle is related to surface roughness.

Hydrophilic cone: surface roughness **reduces** effective contact angle (e.g., from 40°-0°).



Hydrophobic cone: surface roughness **increases** effective contact angle (e.g., from 120°-180°).



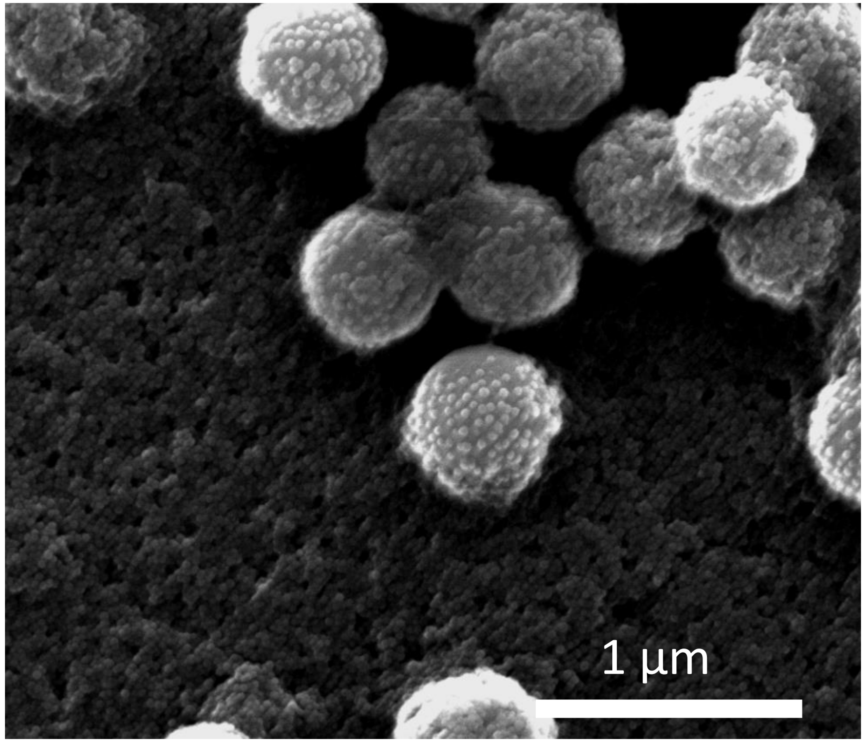


J T Simpson, et.al. (2015). Superhydrophobic materials and coatings: a review. Reports on Progress in Physics, 78(8), 086501.

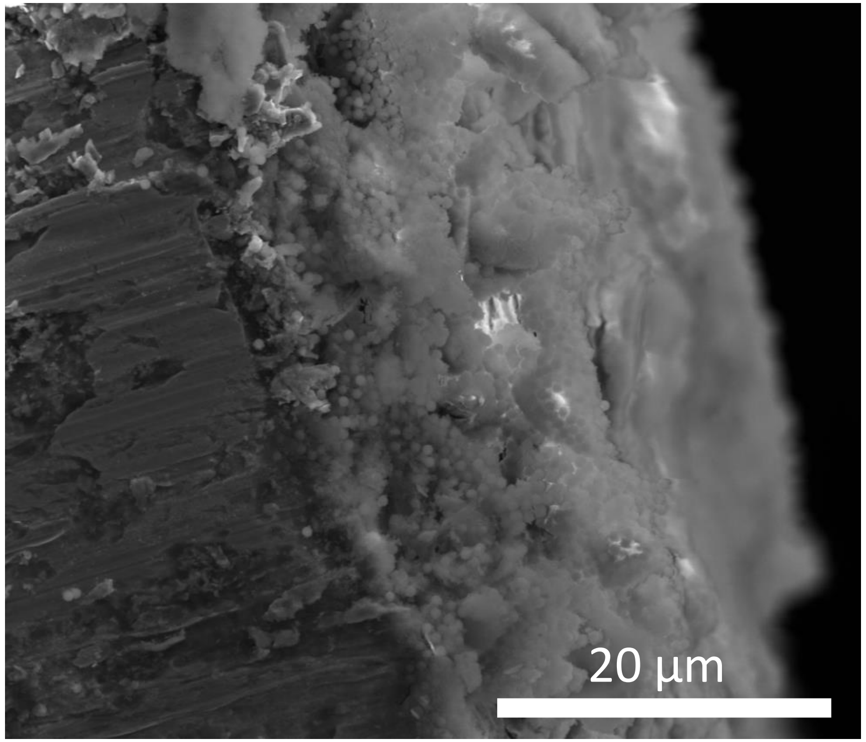
Mixing and Matching Silica Nanoparticles (SiNPs)

Mixing and matching SiNPs of different sizes creates a porous and rough surface.

top view

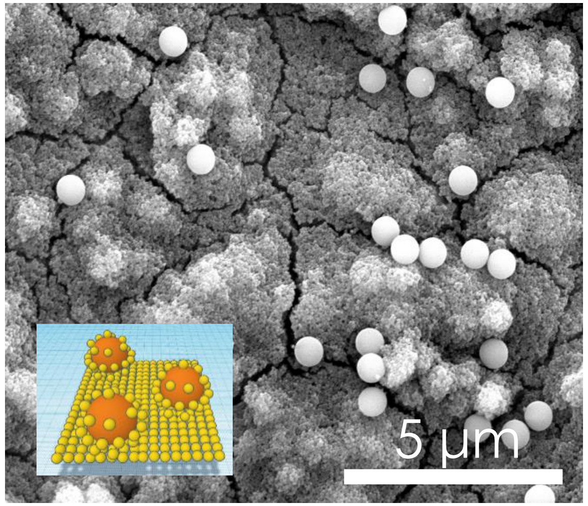


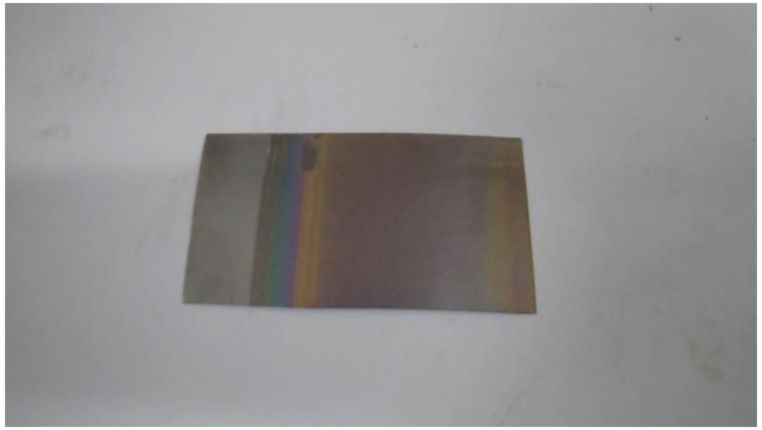
cross-sectional view



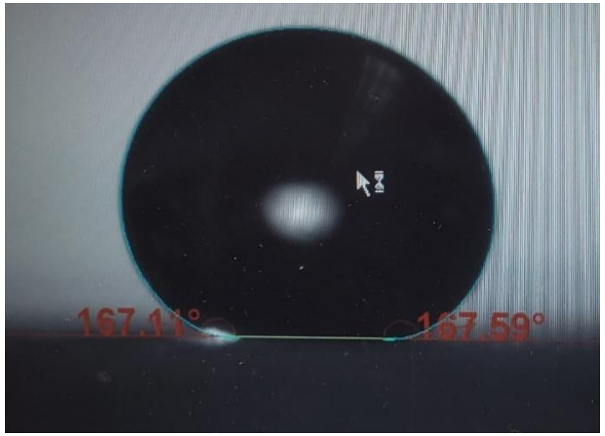
Superhydrophobic Anti-Corrosion Coatings

with mix and match





contact angle > 150°



Soaked in CO_2+3.5wt%NaCl +H_2O for 24 hours

The Influence of the Bottom Primer Layer

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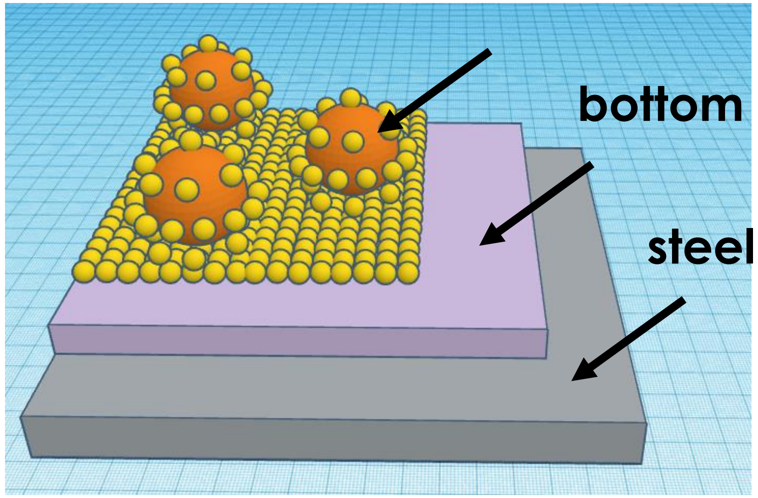
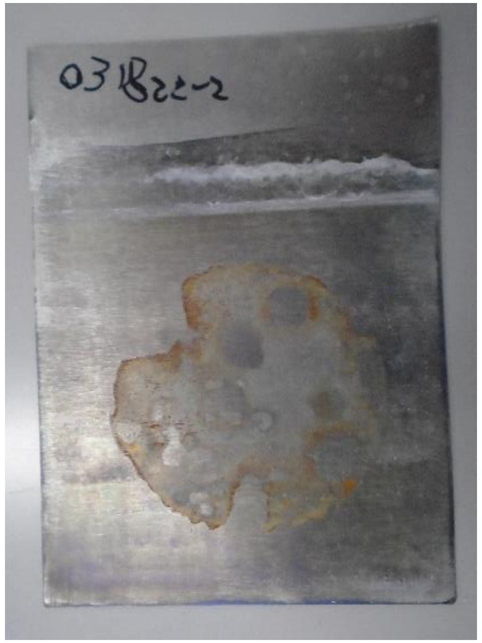


The bottom primer layer also plays a critical role.

soaking in CO_2-saturated salt water for 24 hours

No primer

1st gen primer

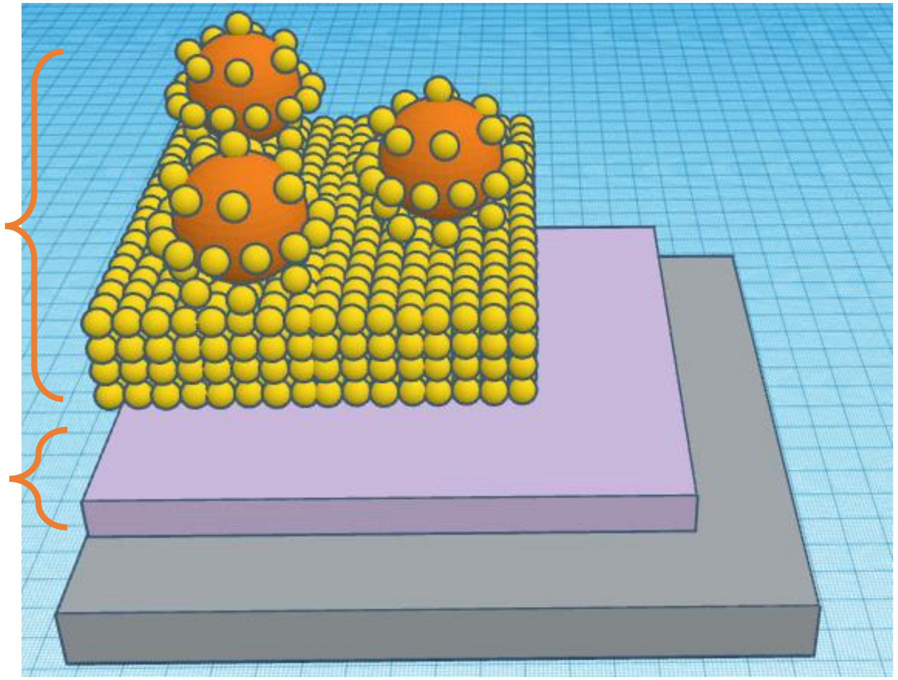


2nd gen primer

Different Layers Serve Different Purposes

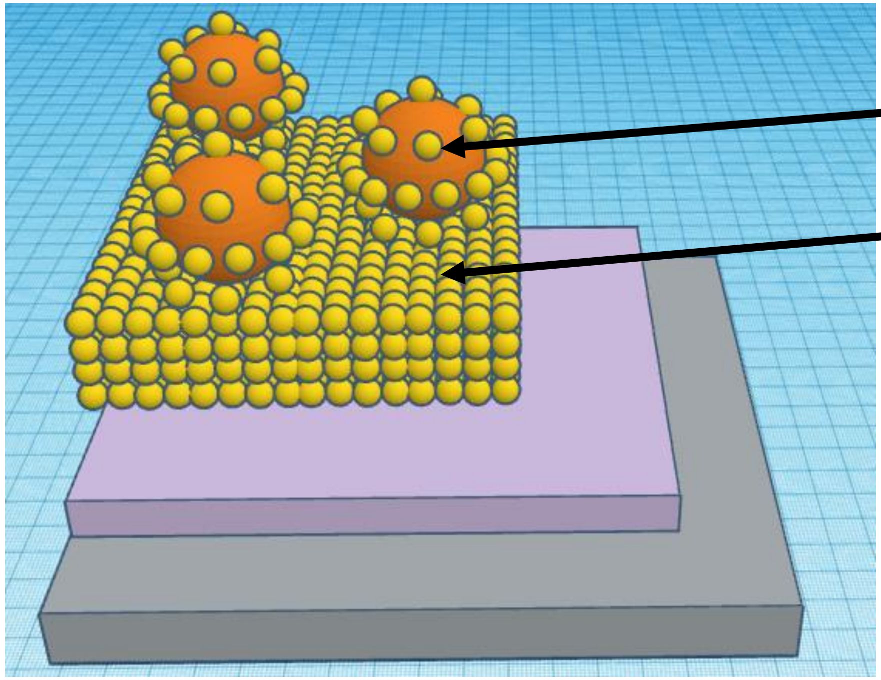
(top) superhydrophobic coating blocks CO_2 and/or NaCl

(bottom) primer layer blocks water vapor



Superhydrophobic Top Layer

The superhydrophobic top layer contains two portions.



Why do we want to mix and match SiNPs?

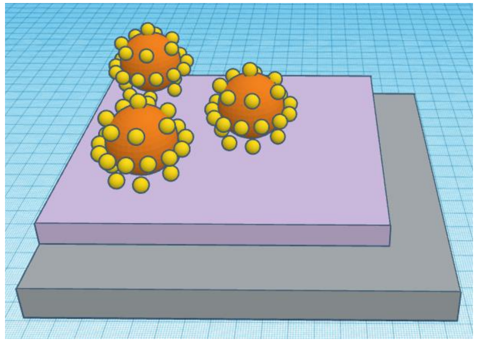
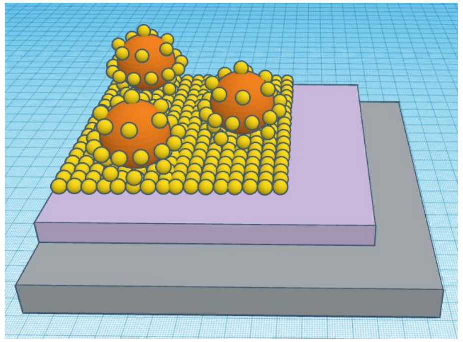
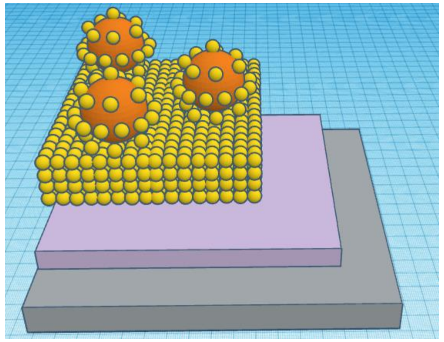
(upper portion) contains small and large SiNPs, and polymer

(lower portion) contains small SiNPs and polymer

Note: Polymer is much smaller than SiNPs, and thus, omitted in the schematic to improve clarity.

Further Optimize Top Hydrophobic Coating

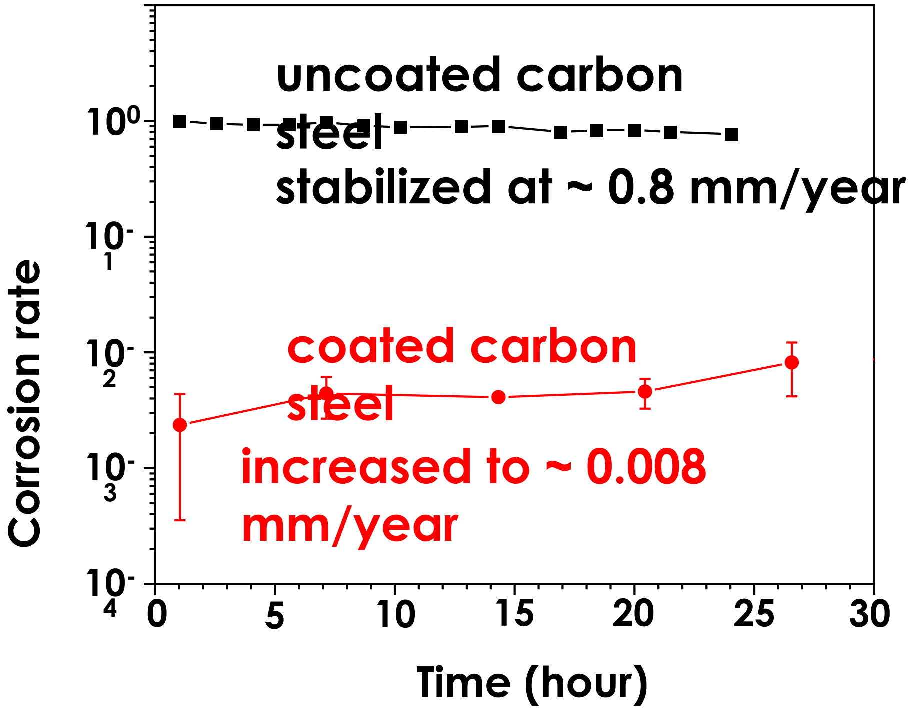
Adding a base layer of smaller silica nanoparticles below the rough upper portion (small and large SiNPs) helps improve corrosion resistance.

	0 bilayer	1 bilayer	4 bilayers
# of polymer/small SiNPs bilayers			
soaking in CO_2-saturated salt water for 24 hours			

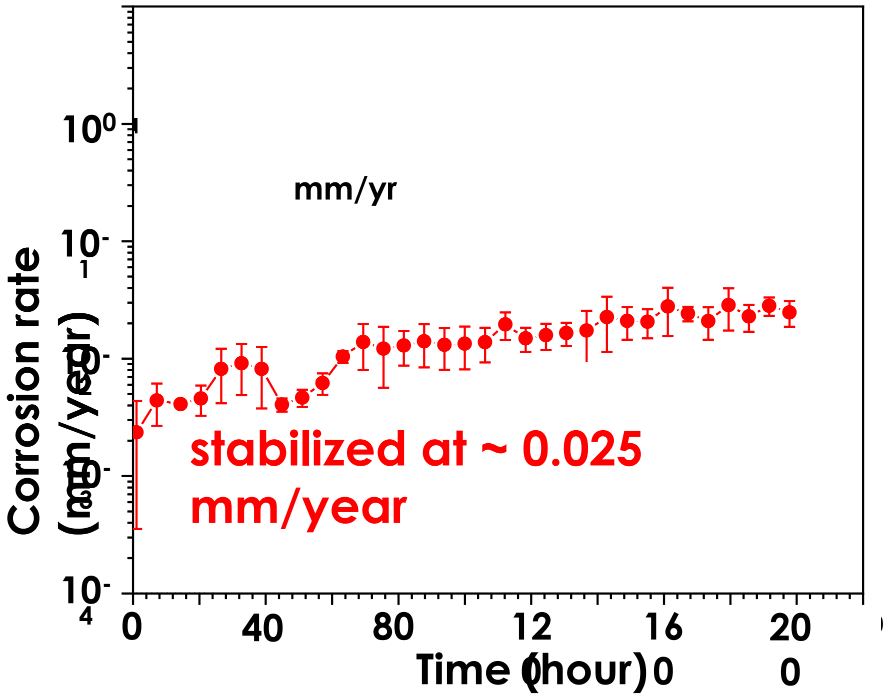
Anti-Corrosion Performance for CO_2+NaCl+H_2O

The corrosion rate was first analyzed using linear polarization resistance.

Short-term test



Long-term test



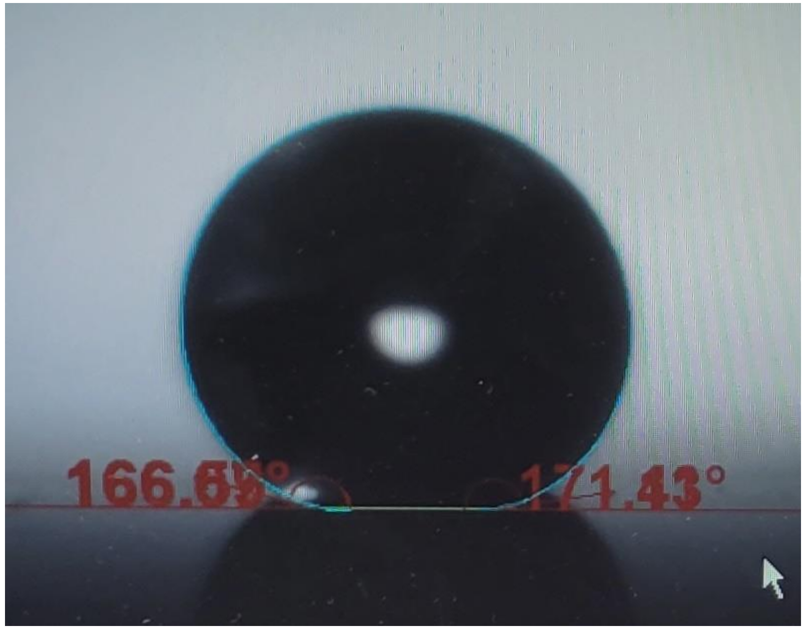
Electrochemical tests performed by Zineb Belarbi. Testing temperature=20 °C; 3.5wt% NaCl; CO_2 bubbling.

Mechanical Test

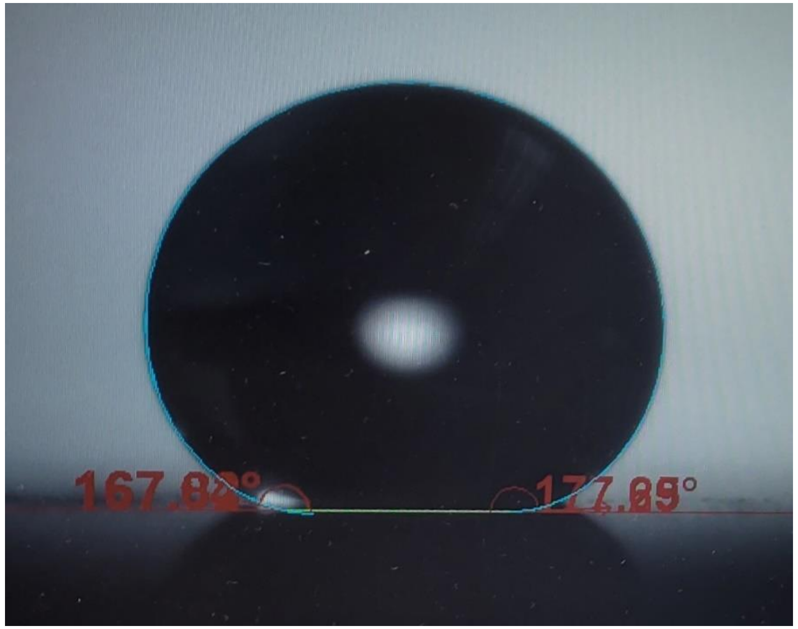
Durability of coating was tested according to ASTM D3359 (scratch and then peel with adhesive tape).

The coating remained superhydrophobic

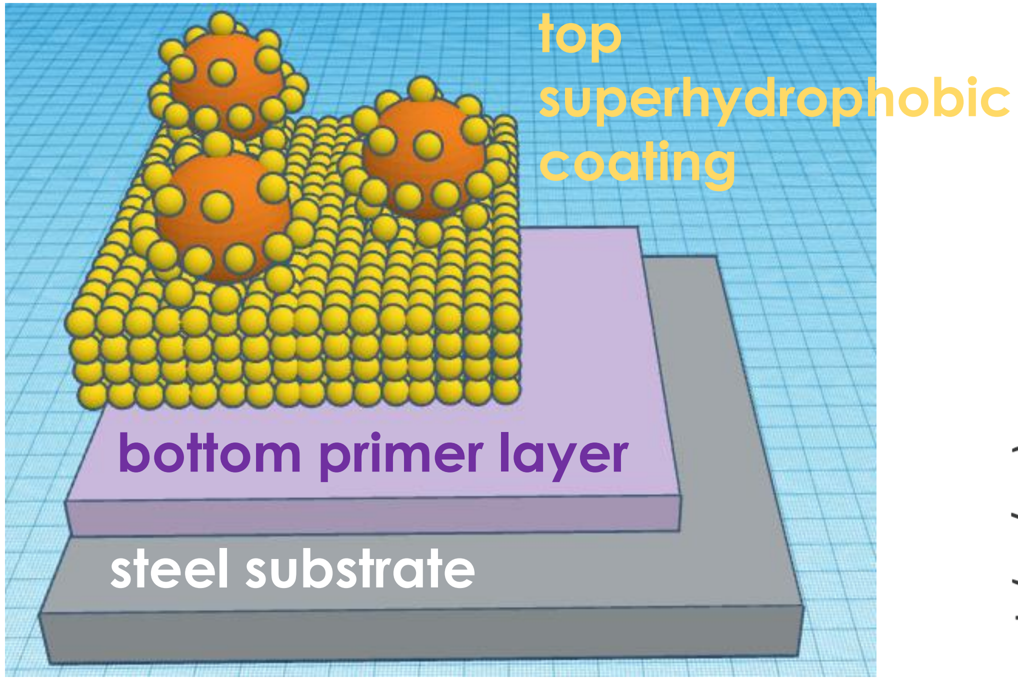
before

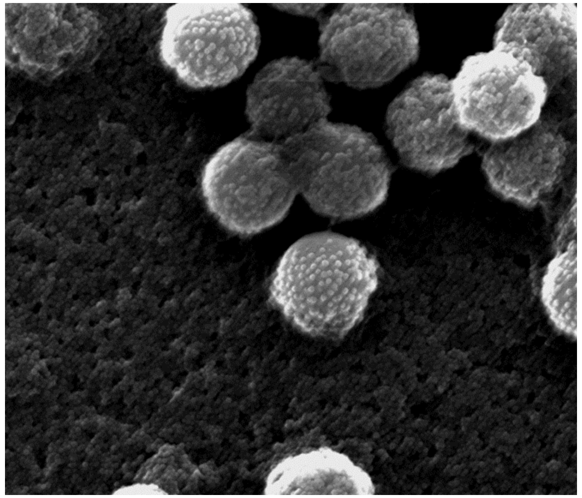


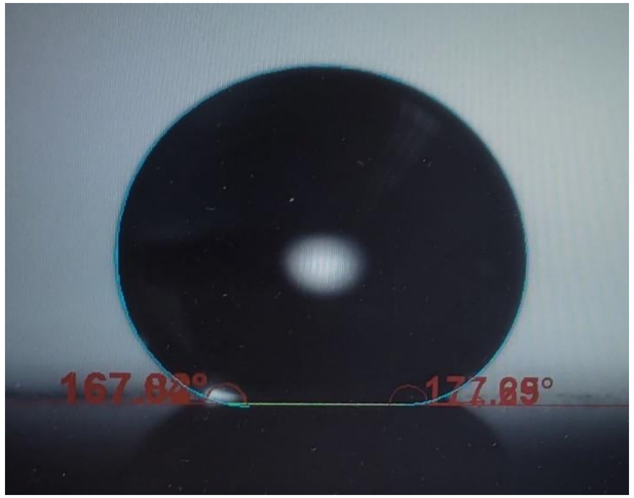
after

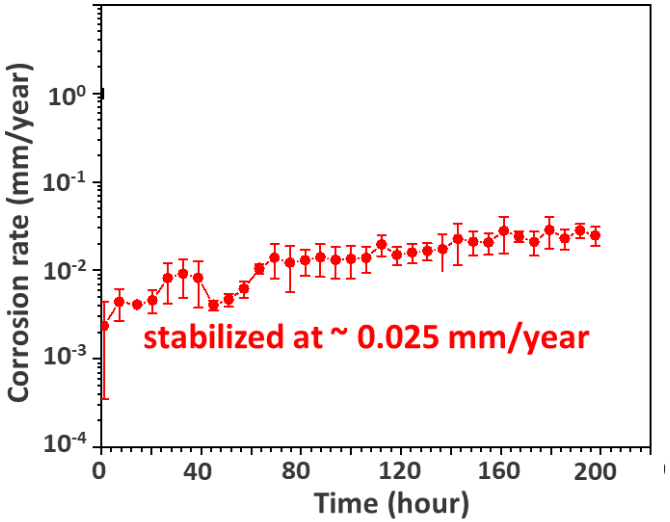


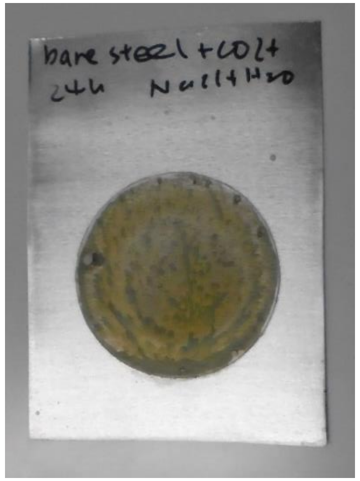
Conclusions











uncoated

coated

Acknowledgements

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