Mitigation of MIC from the material and its surface

Dake Xu, Professor

Eurocorr 2017, Prague, Czech

Background

- BS and MS in Bioengineering

Microbiology, Molecular biology

- Ph.D, Institute for Corrosion and Multiphase Technology, Ohio University, 2008-2013 Ph.D advisor: Tingyue Gu

Corrosion, Bioelectrochemistry

- Associate Professor, Institute of Metal Research, Chinese Academy of Sciences, 2013-2017

Material, Electrochemistry

- Professor, Northeastern University (China), 2017

- Research interests: Biocorrosion, antibacterial material and biomaterial, biofilm and biocide. Mainly focused in the mechanism and mitigation of marine MIC and biofouling.
- Published more than 50 peer-review MIC-related journal papers.
- Editorial board member of NPJ Material degradation.
- 6 Ph.D and 12 master students in my group (3 international graduate students).


HYS

Significant works

Extracellular electron transfer (EET) in microbial fuel cell (MFC)

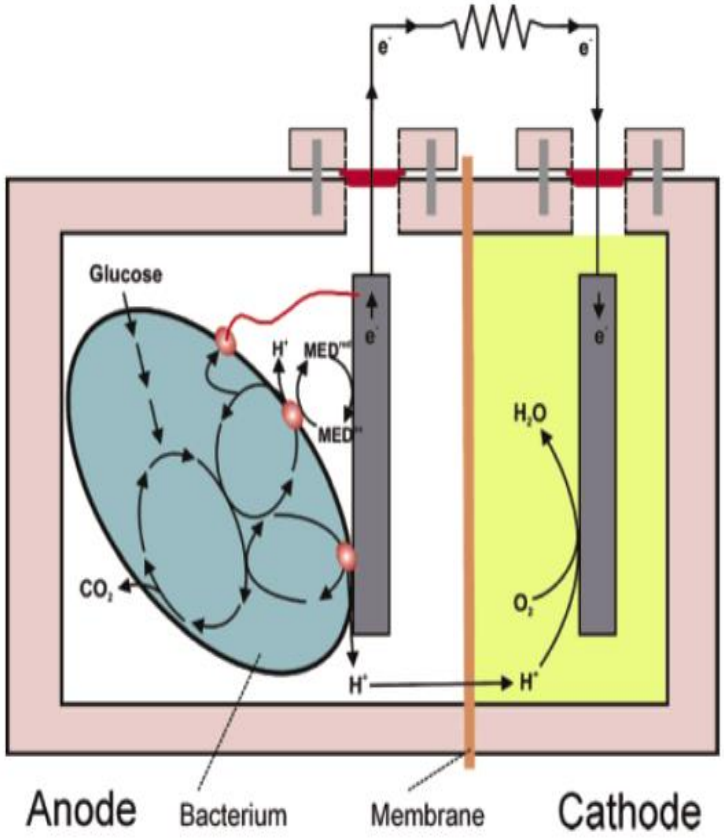
1. Direct Electron Transfer (DET)

Direct cell wall-metal surface contact

Pili (conductive nanowires).

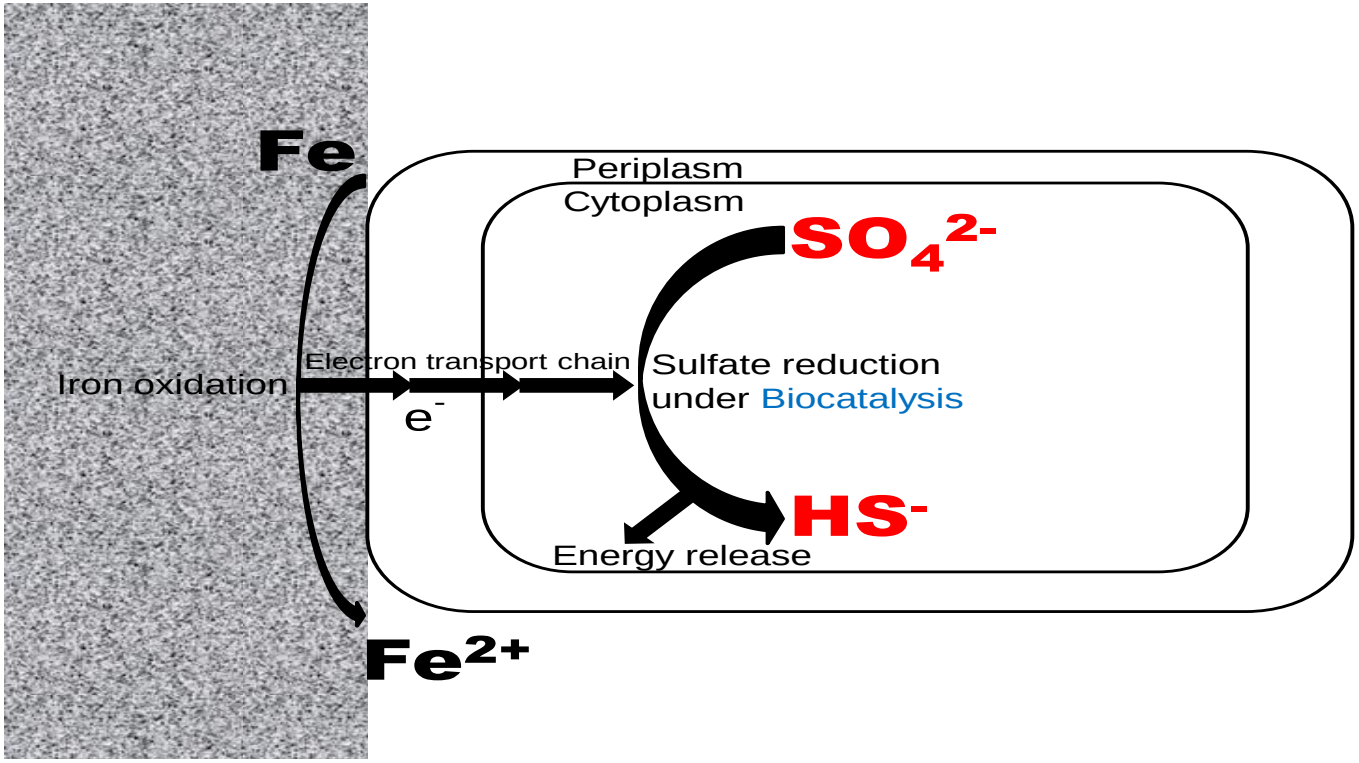
2. Mediated Electron Transfer (MET)

FAD and riboflavin can act as electron shuttles. Some other chemicals such as H_2 are also used as electron carriers.



✓ MIC is analogous to the biocathode process of MFC.

Theory



Biocatalytic cathodic sulfate reduction (BCSR) by sessile sulfate-reducing bacteria (SRB) on the iron surface:

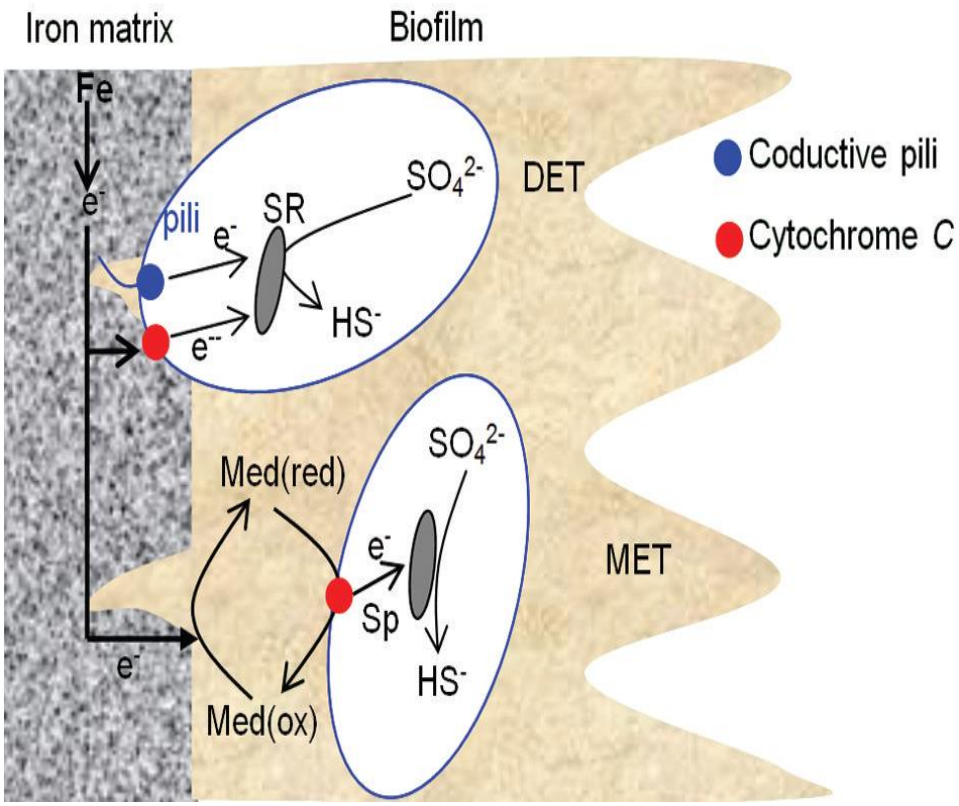
Anodic: $4Fe \rightarrow 4Fe^{2+} + 8e^-$

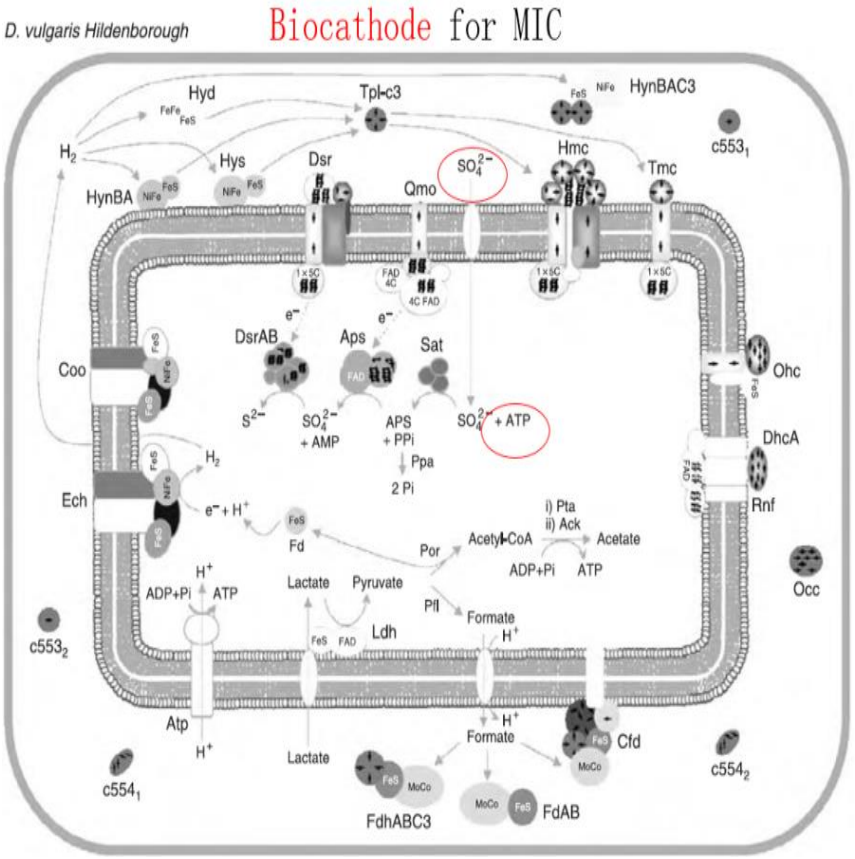
Cathodic: $SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$

Mechanism for MIC by SRB utilization of electrons from iron oxidation for sulfate reduction. BCSR can explain why and how MIC due to SRB happens.

1. EET explains how MIC occurs

The cathodic reactions take place in the cytoplasm of the corrosive bacteria, which is defined as "biocathode"in MFC.

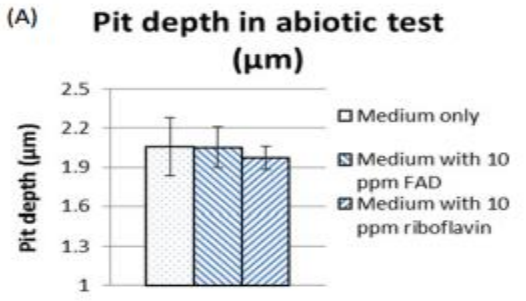


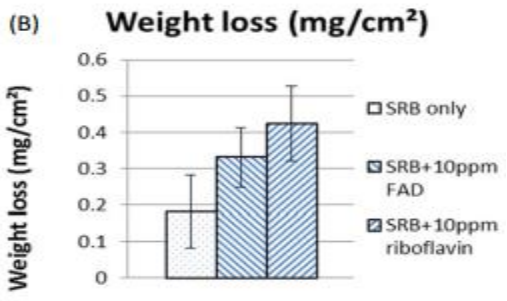


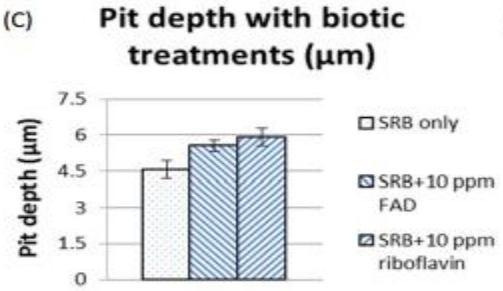
✓ EET is the key to investigate the MIC mechanisms.

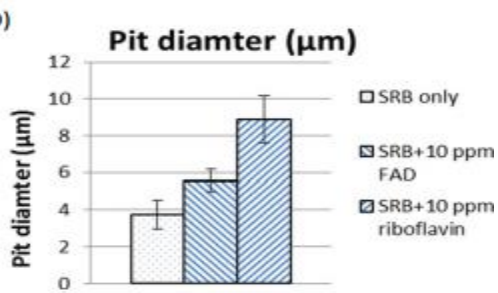
1. EET explains how MIC occurs

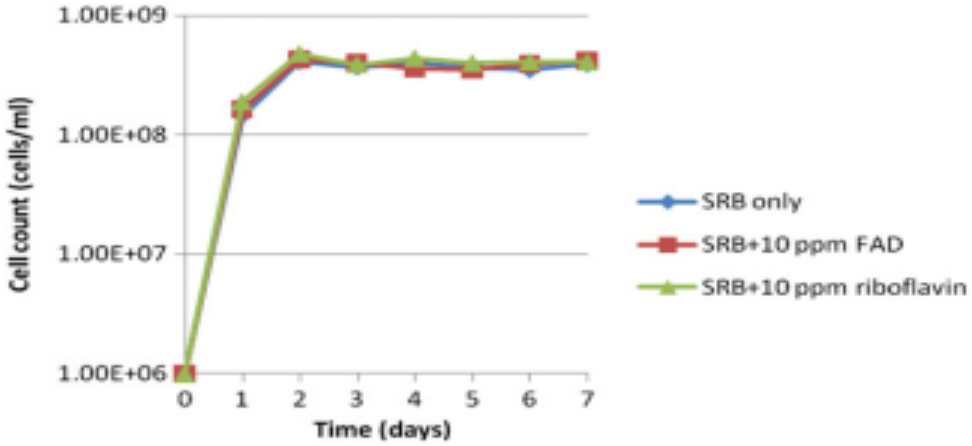
Electron mediators promote MIC caused by SRB

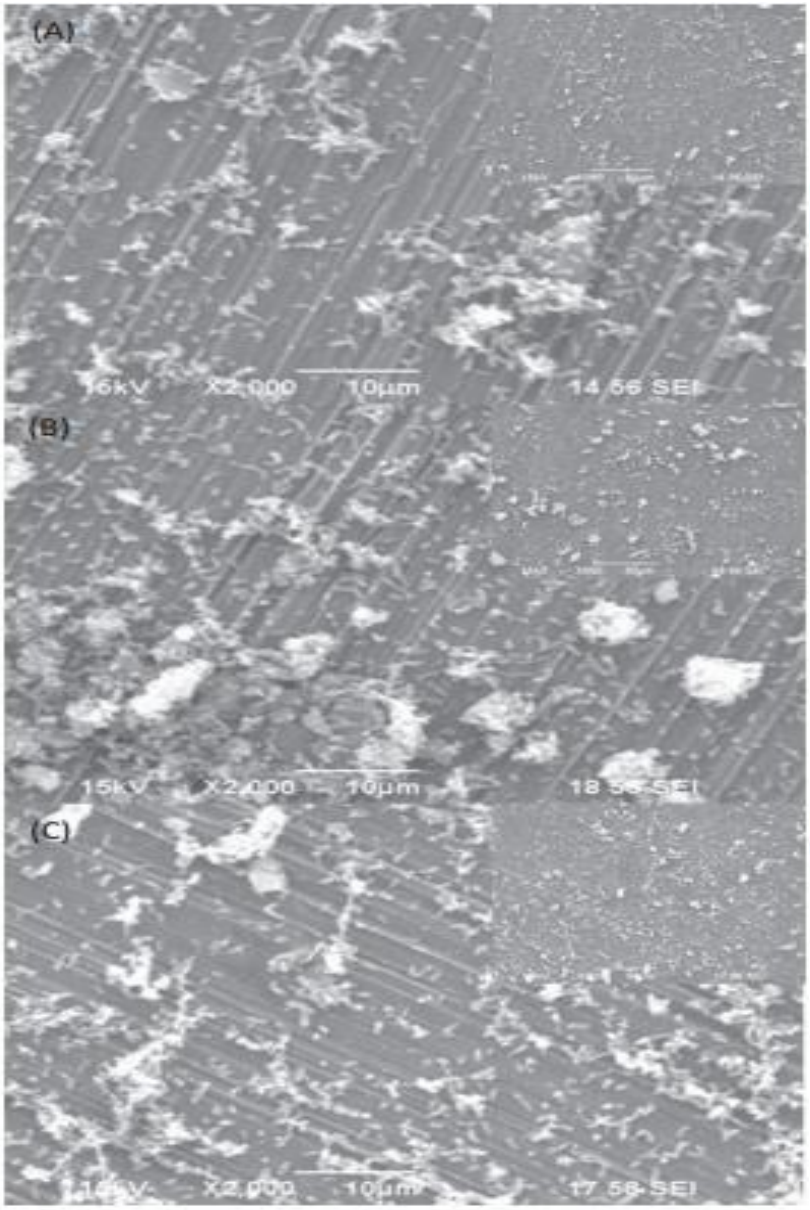








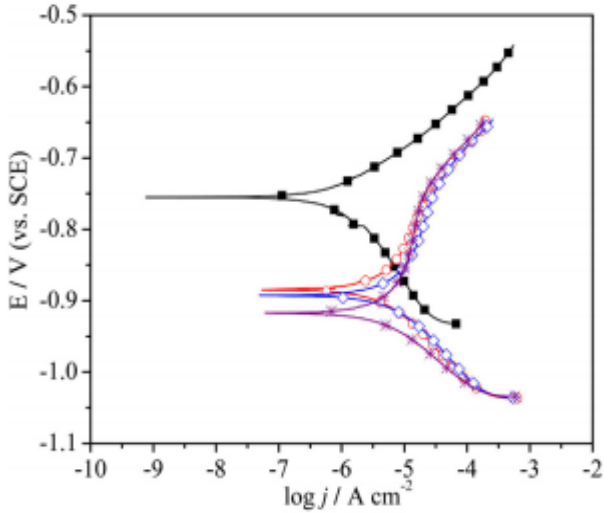


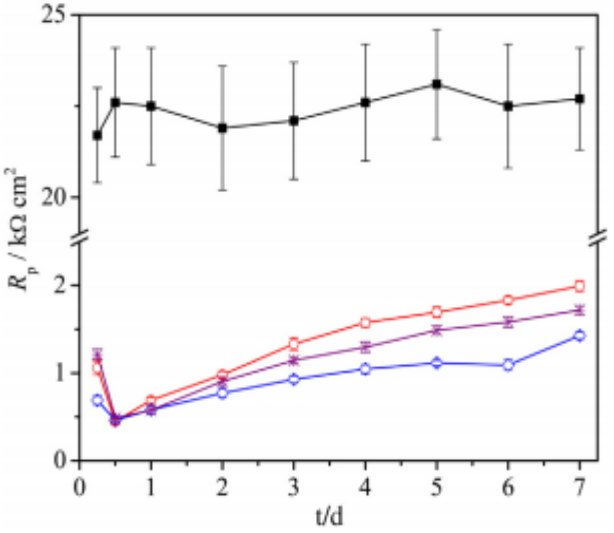


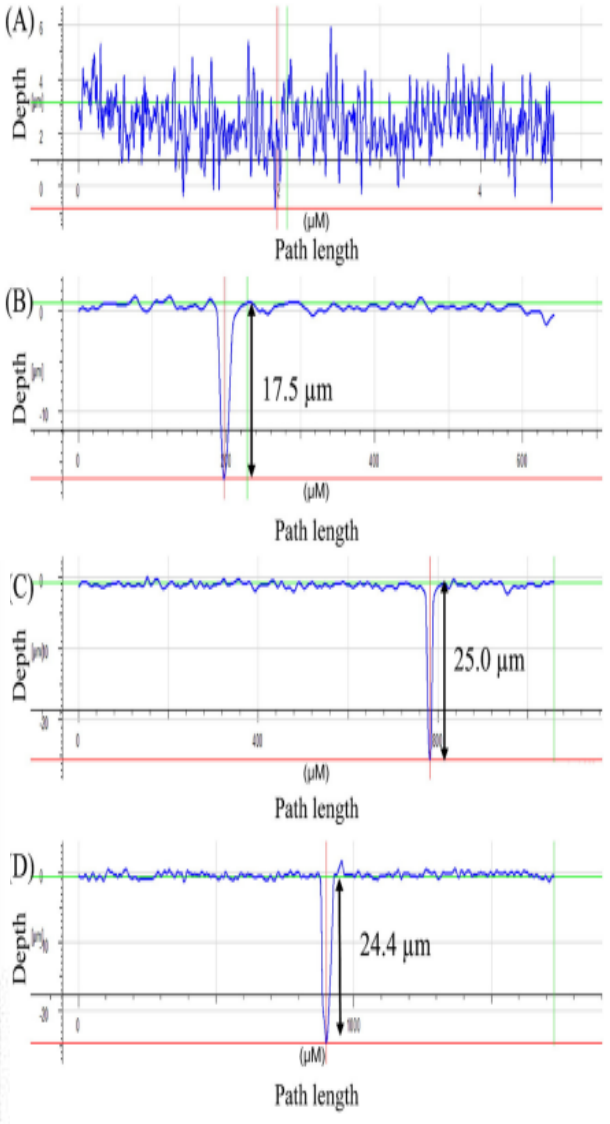
Bioelectrochemistry, 101:14-21, 2015

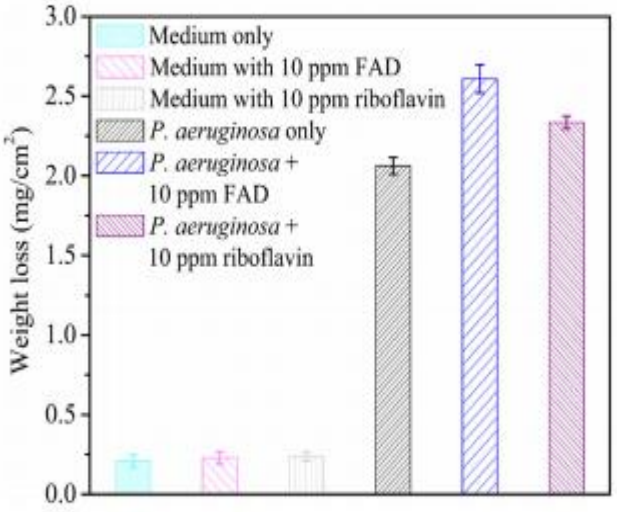
1. EET explains how MIC occurs

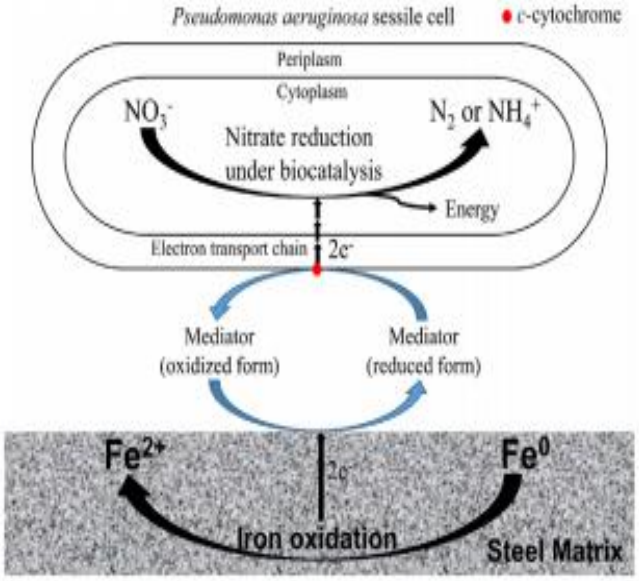
Electron mediators promote MIC caused by Nitrate-reducing bacteria (NRB)





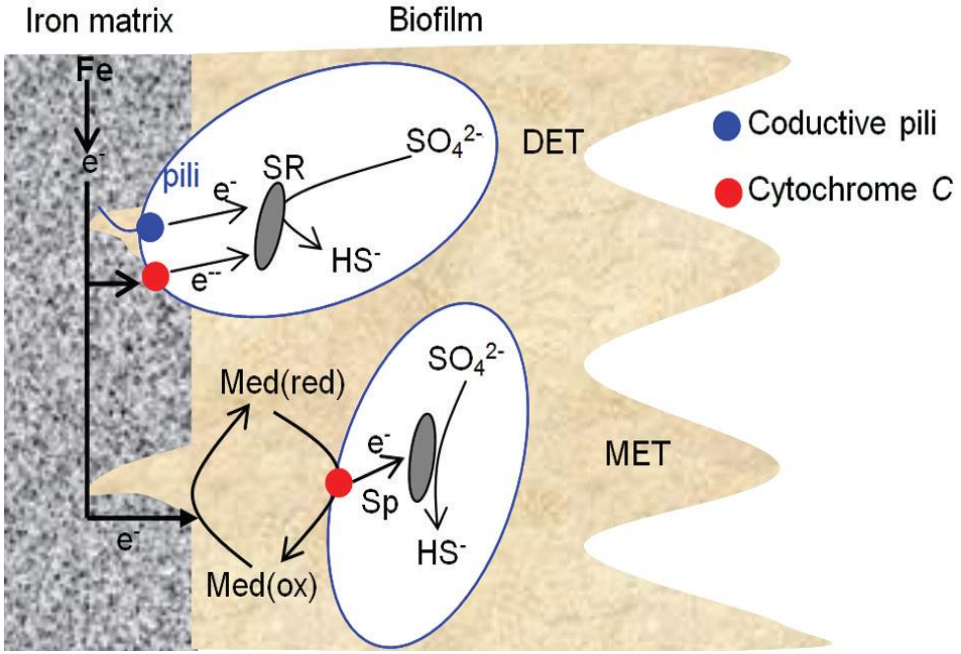






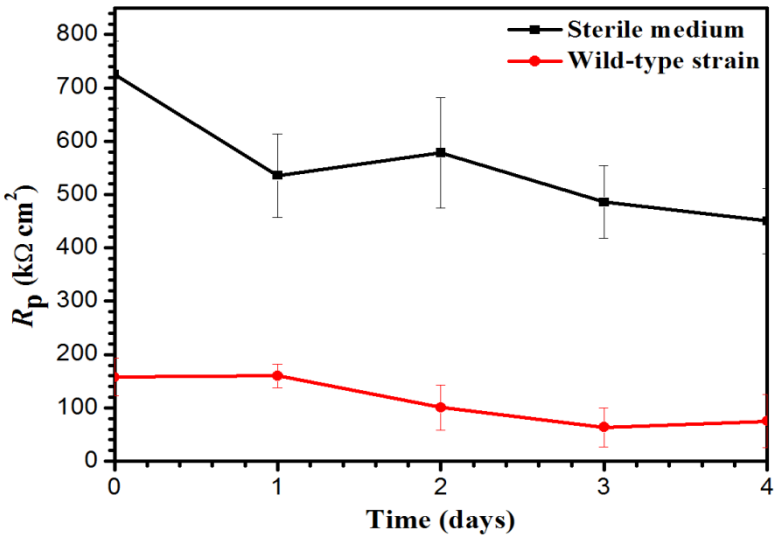
Bioelectrochemistry, 118:38-46, 2017

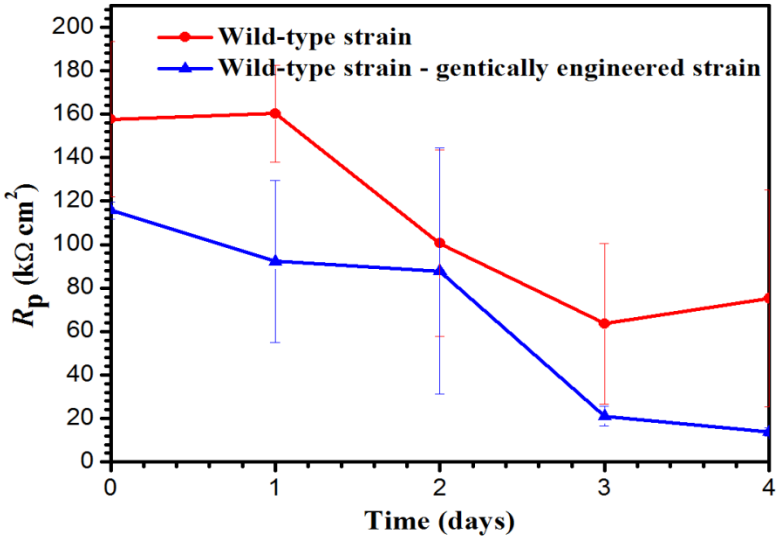
Breakthrough (Proof of EET in MIC)



We found the genes that determined the expression of electron mediators. Then we overexpressed these genes using synthetic microbiology methods to figure out if MIC was accelerated.

Work in progress!!!





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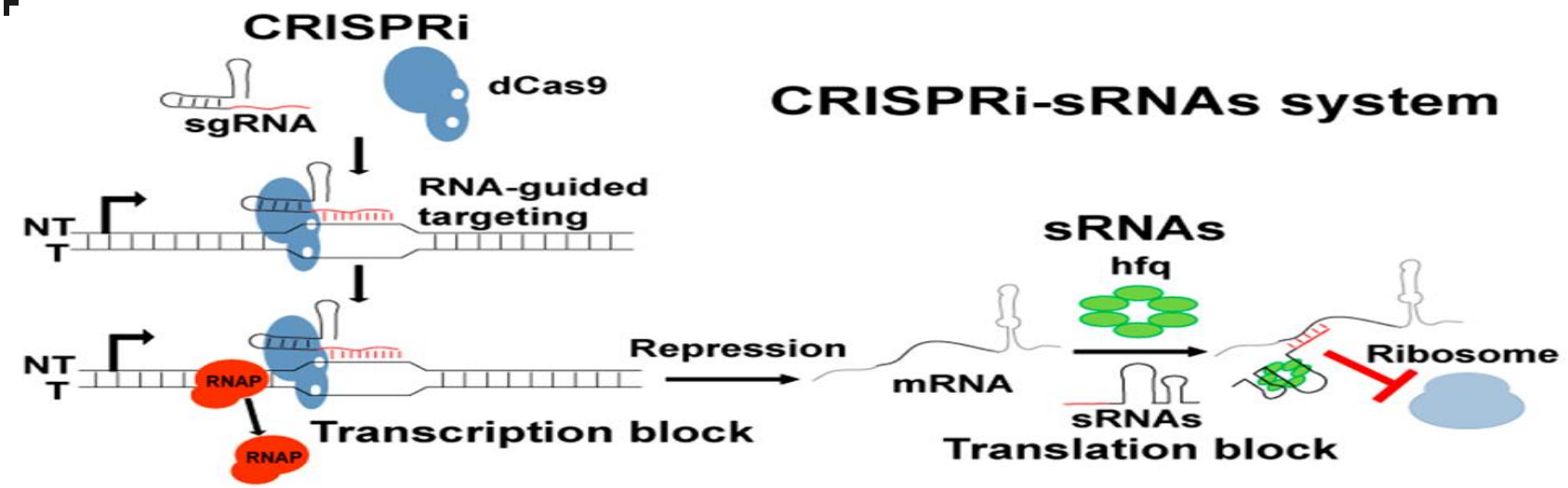

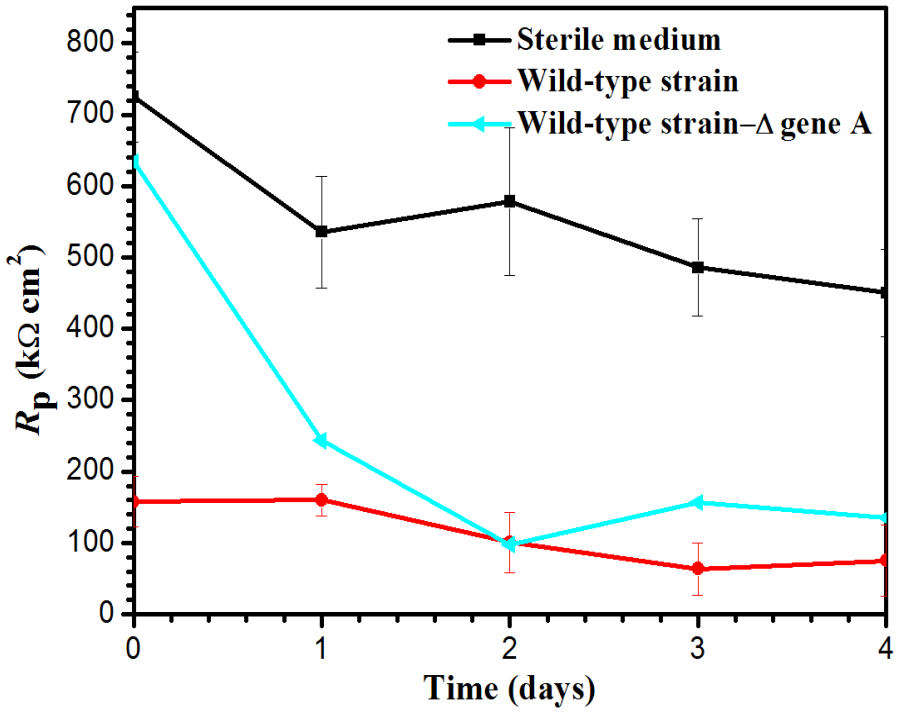

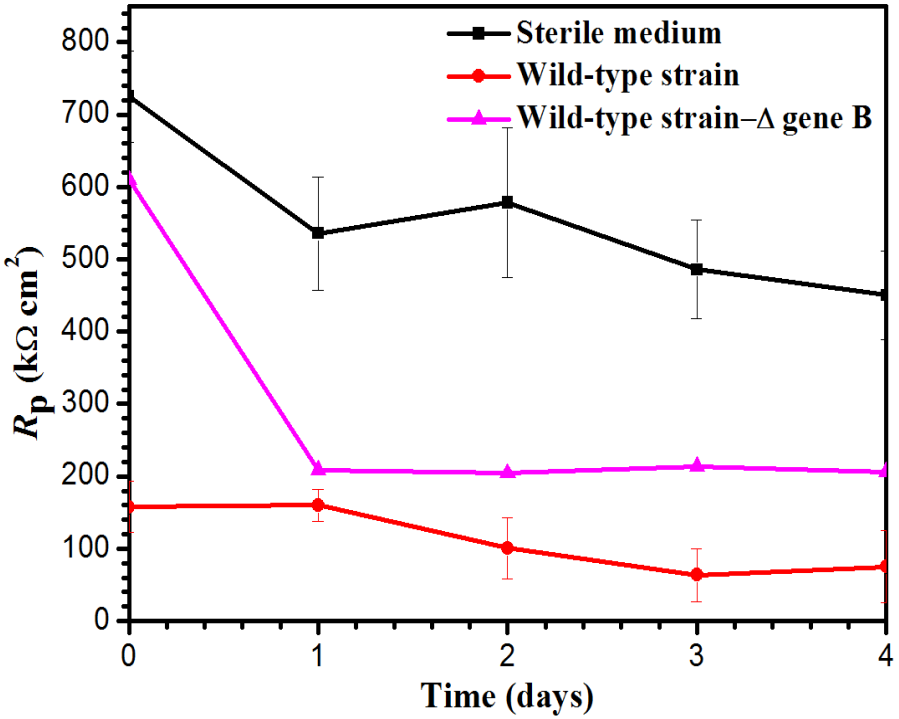

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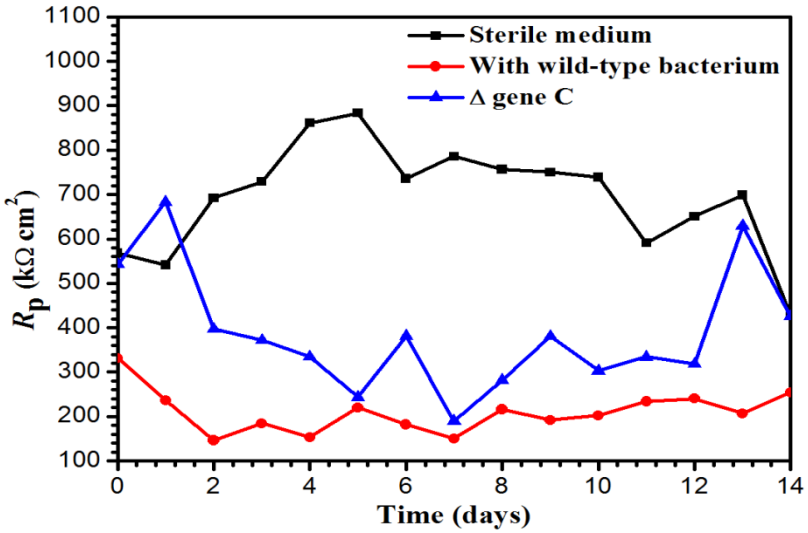
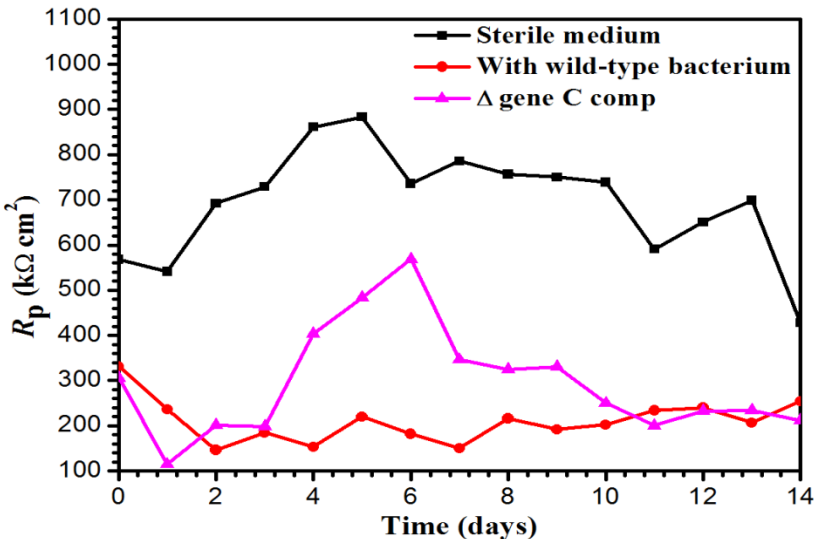
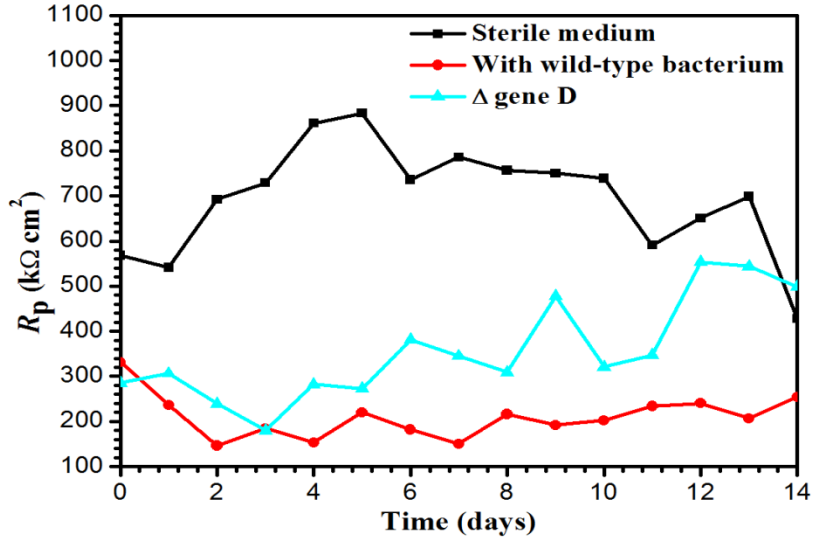
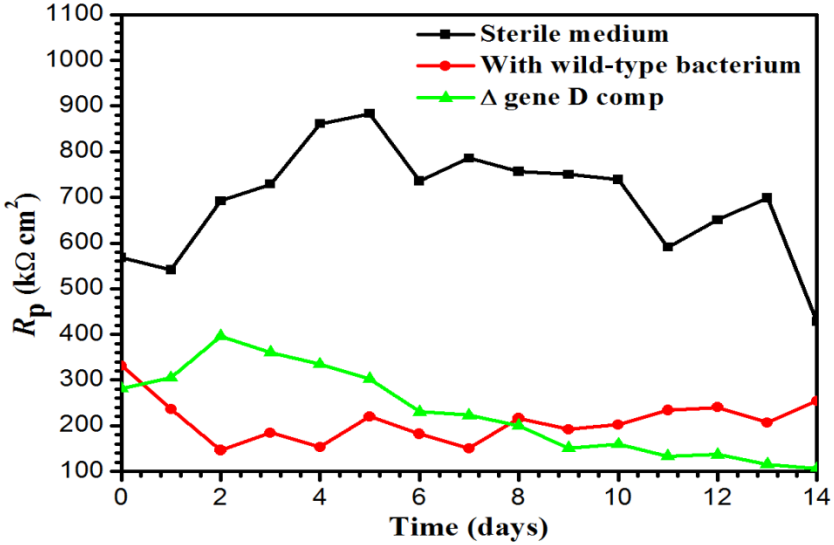








Another electroactive biofilm confirmed the important role of MET in MIC process.

✓ MET was proved in MIC from genetic level.

2. Bioenergetics explains why MIC occurs

Redox couple		n	E°′ (Mv)
$2CO_2$ + 2acetate /hexose		8	−670
Fe^{2+}/Fe^{0}	←	2	−447
CO_2 + acetate/lactate		4	−430
CO_2 /formate		2	−432
$2H^+/H_2$		2	−414
			(−270 to −300)[a]
Acetate/ethanol		4	−390
CO_2/methanol		6	−370
2Acetate/butyrate		4	−290
$2CO_2$ /acetate		8	−290
CO_2/CH_4		8	−244
SRB SO_4^{2-}/HS^-	→	8	−217 (−200)[c]
Fumarate/succinate		2	+33
NO_2^-/NH_3		6	+330
NO_3^-/NH_3		8	+360
NRB ? ? ? NO_3^-/NO_2^-	→	2	+430
$2NO_3^-/N_2$		10	+760
$O_2/2H_2O$		4	+818
$H_2O_2/2H_2O$		2	+1350

NO_3^-/NH_4^+ = 358 mV

+447 mV

Redox Couple

+360 or +760 mV

$E^{o'}$ = 807 mV or 1207 mV

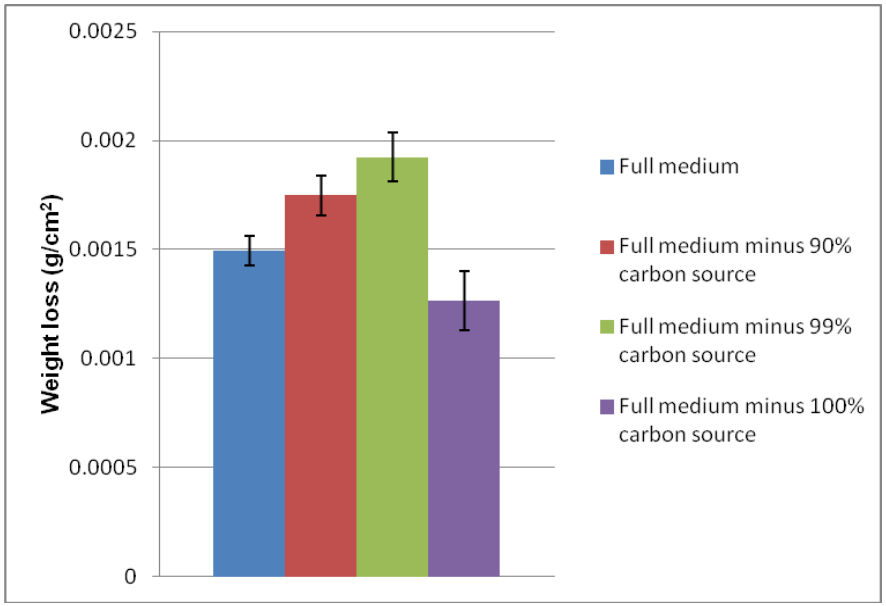
$\Delta G^{o'} = -nFE^{o'} < 0$

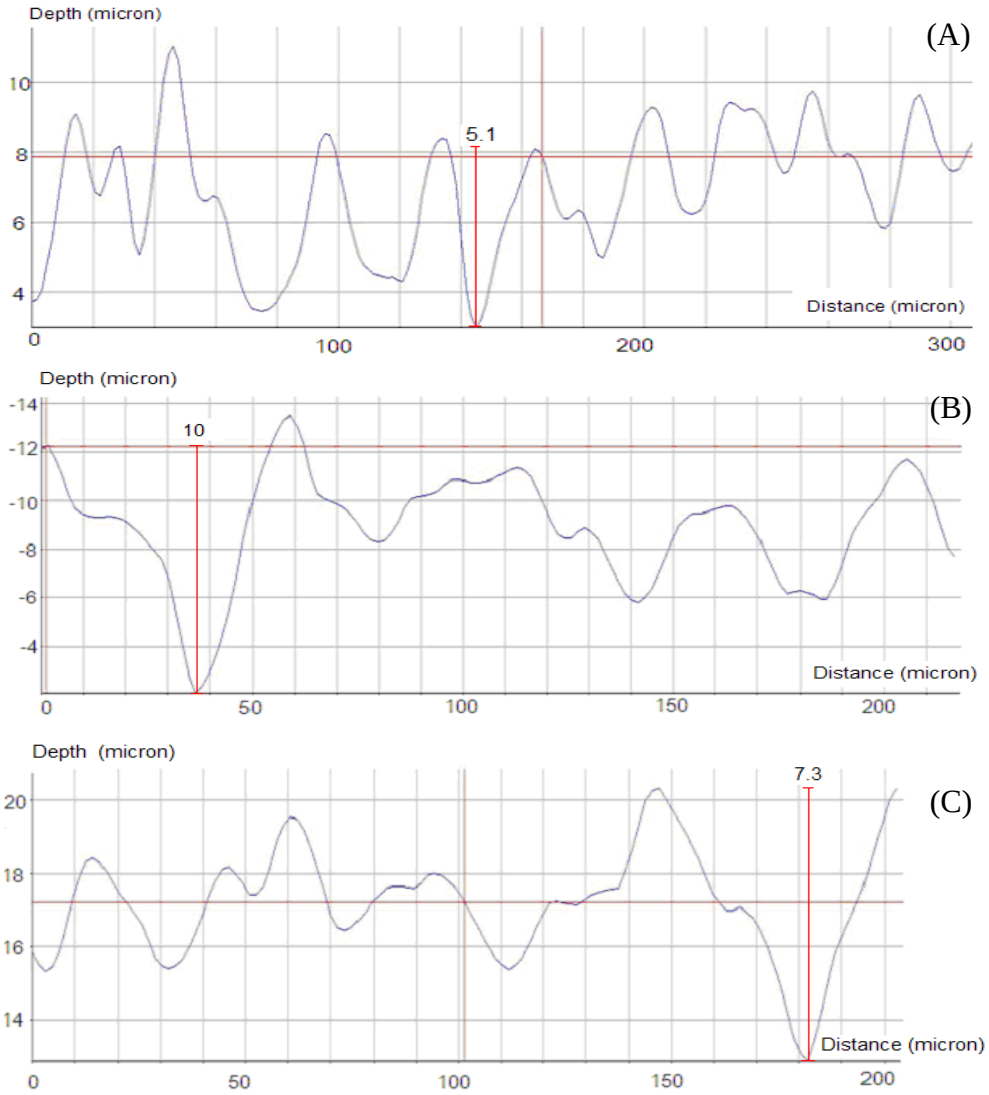
- ✓ Electrogenic bacteria corrode for maintenance energy.
- ✓ NRB is corrosive, and should be more aggressive than SRB.

2. Bioenergetics explains why MIC occurs

Starvation of organic carbon accelerates MIC due to SRB （Field condition）

Medium	Sessile Cell Count (cells/cm^2)
Full medium (ATCC 1249 Medium)	≥10^6
Full medium minus 90% carbon source	≥10^5
Full medium minus 99% carbon source	≥10^4
Full medium minus 100% carbon source	≥10^4

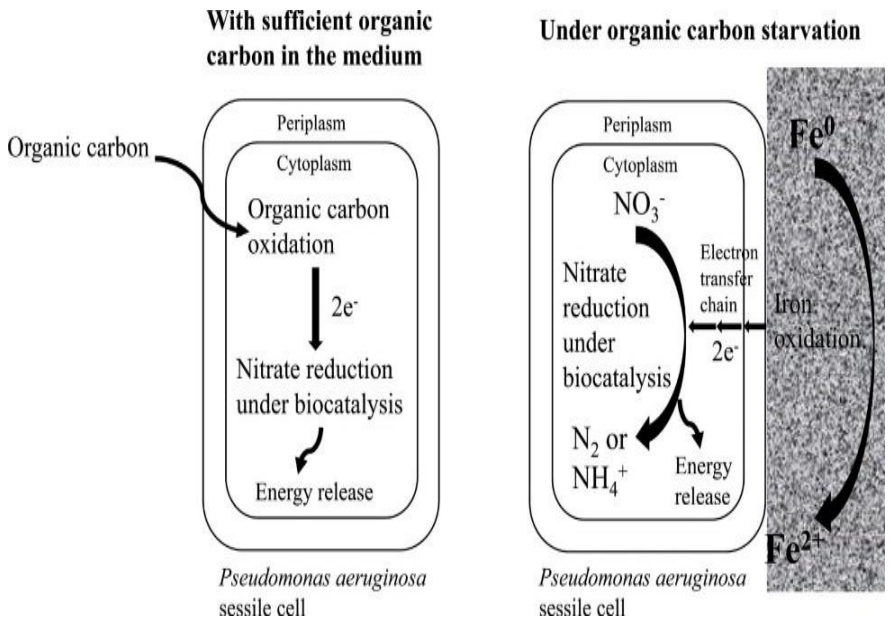


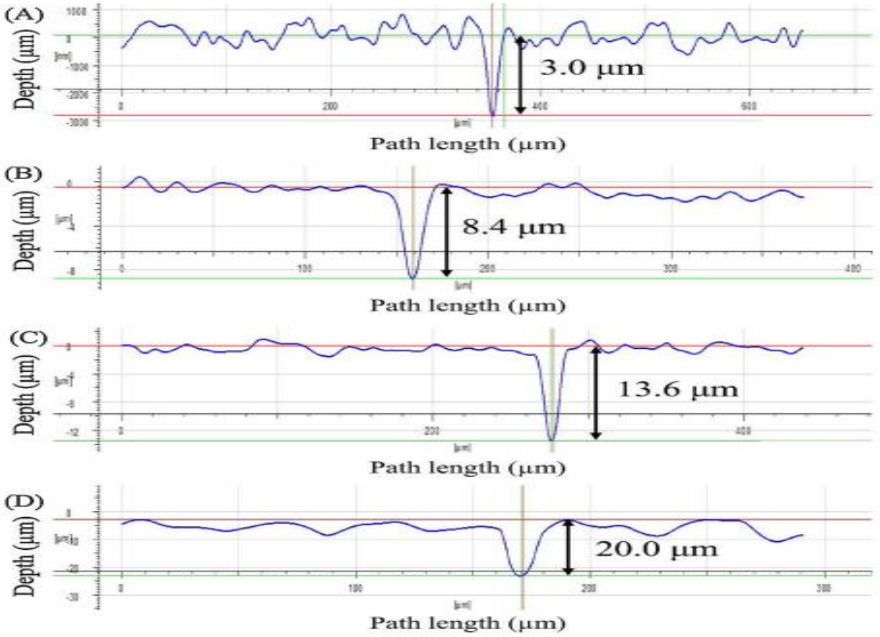


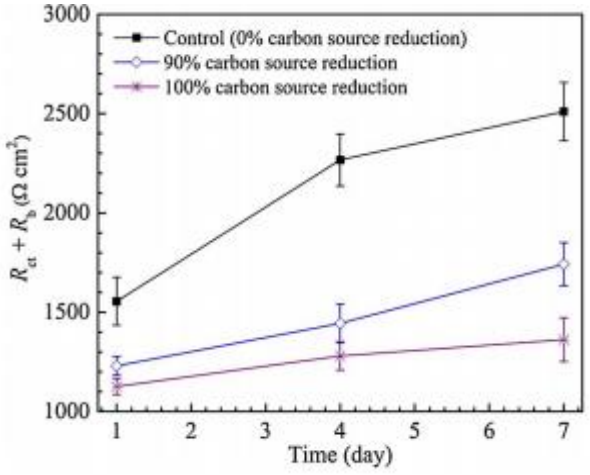
Int Biodeterior Biodegrad, 91:74-81, 2014

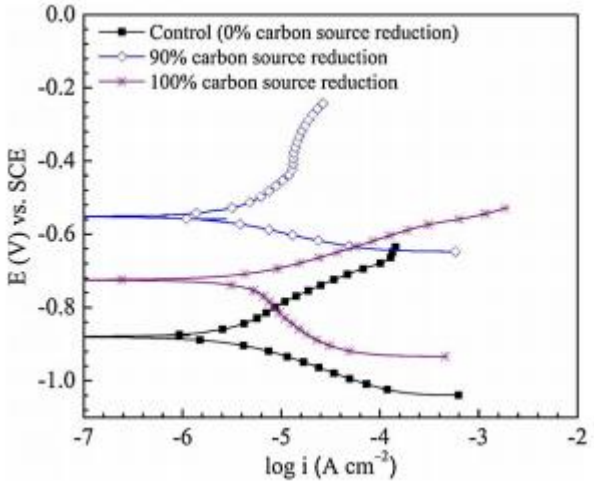
2. Bioenergetics explains why MIC occurs

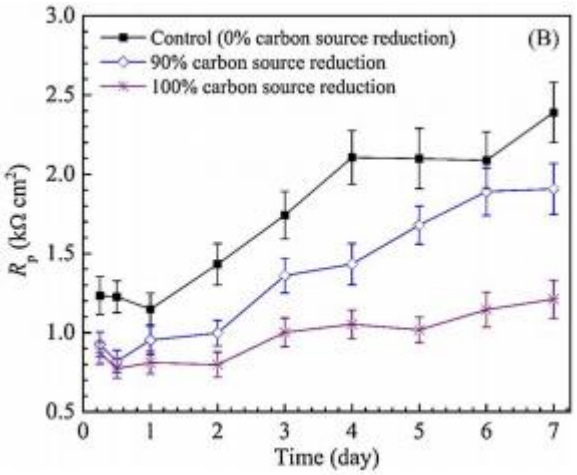
Starvation of organic carbon accelerates MIC due to NRB





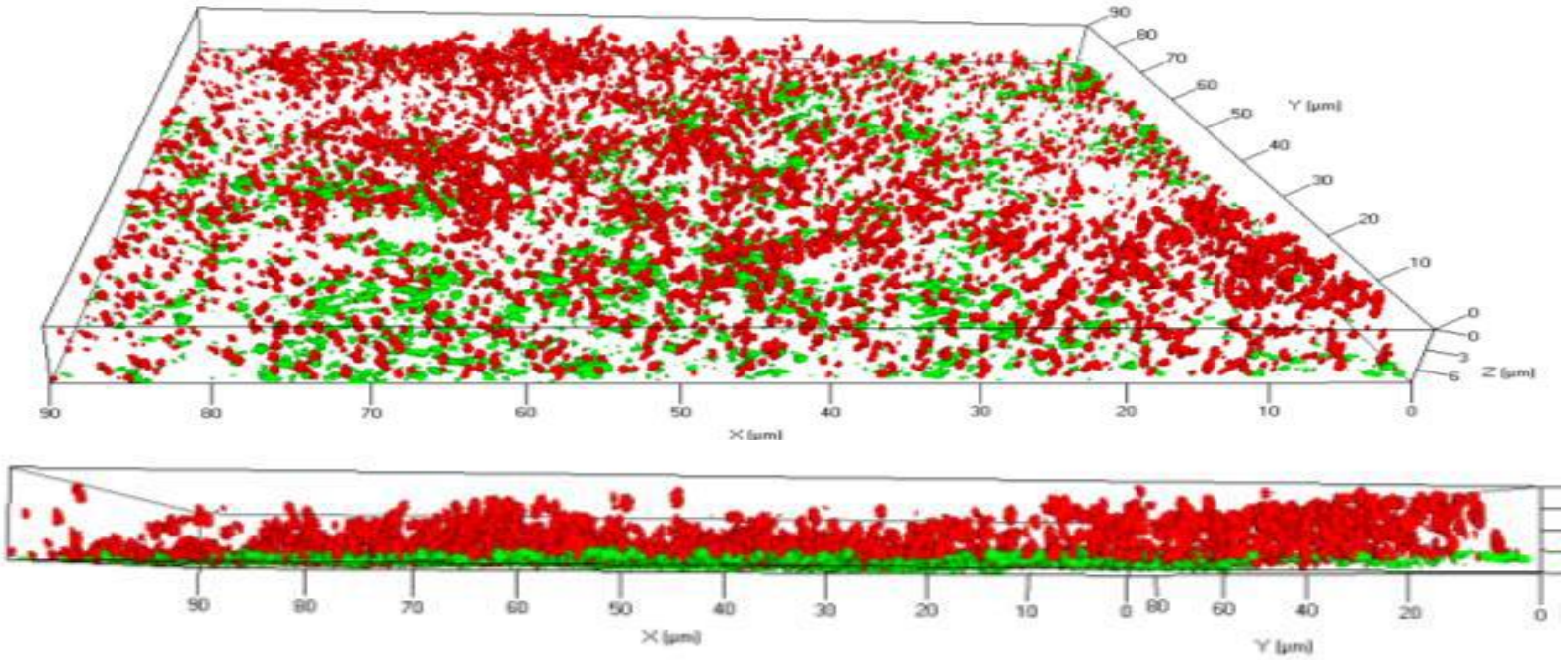






Corrosion Sci. 2017

2. Bioenergetics explains why MIC occurs



In the absence of organic electron donors, the sulfate reducing Bacterium *D. vulgaris* could survive for a long period, up to 55 days.

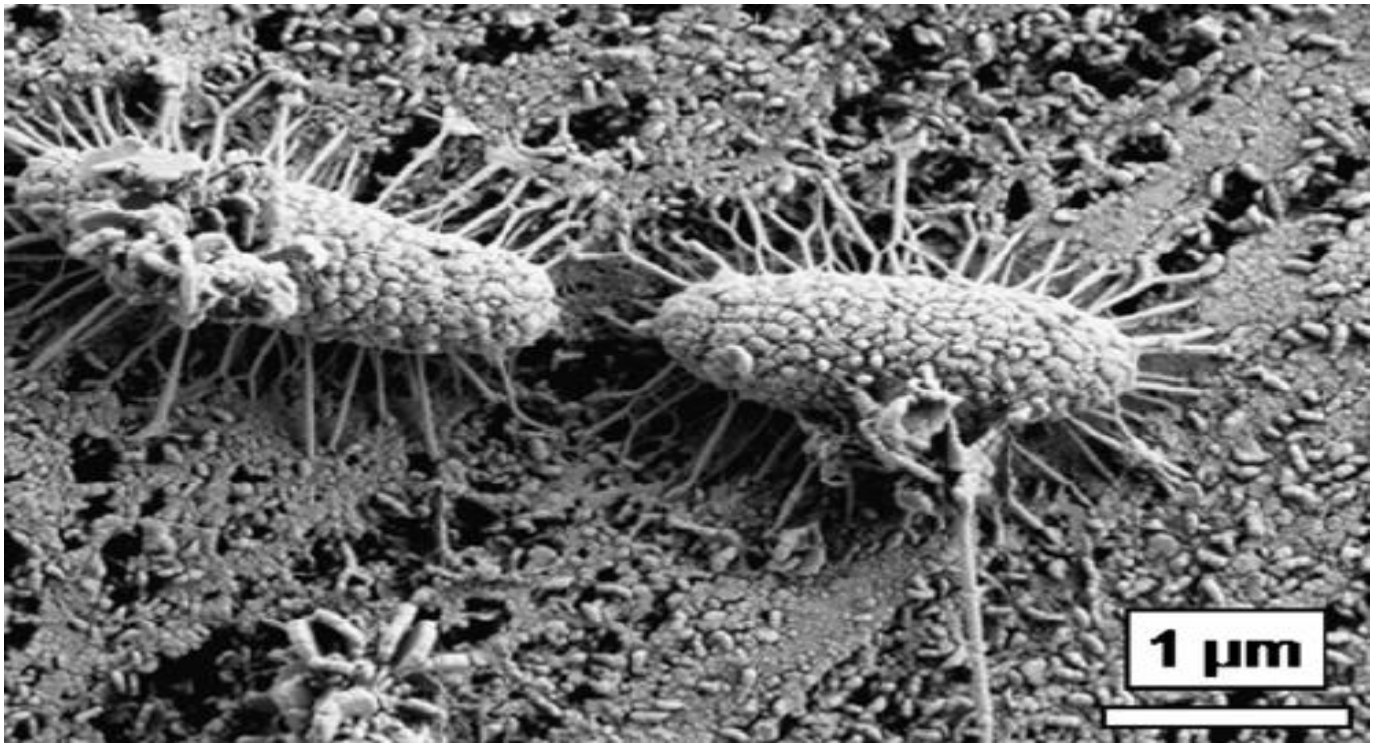
Only when the methanogenic strains are deprived of energy sources such as organic carbon, they start to turn aggressive towards carbon steel, causing increased corrosion, indicating that the phenomenon is likely not strain specific.

Corrosion Sci,90:89-100, 2015
Corrosion Sci,119:102-111, 2017

2. Bioenergetics explains why MIC occurs

On-demand electron transfer

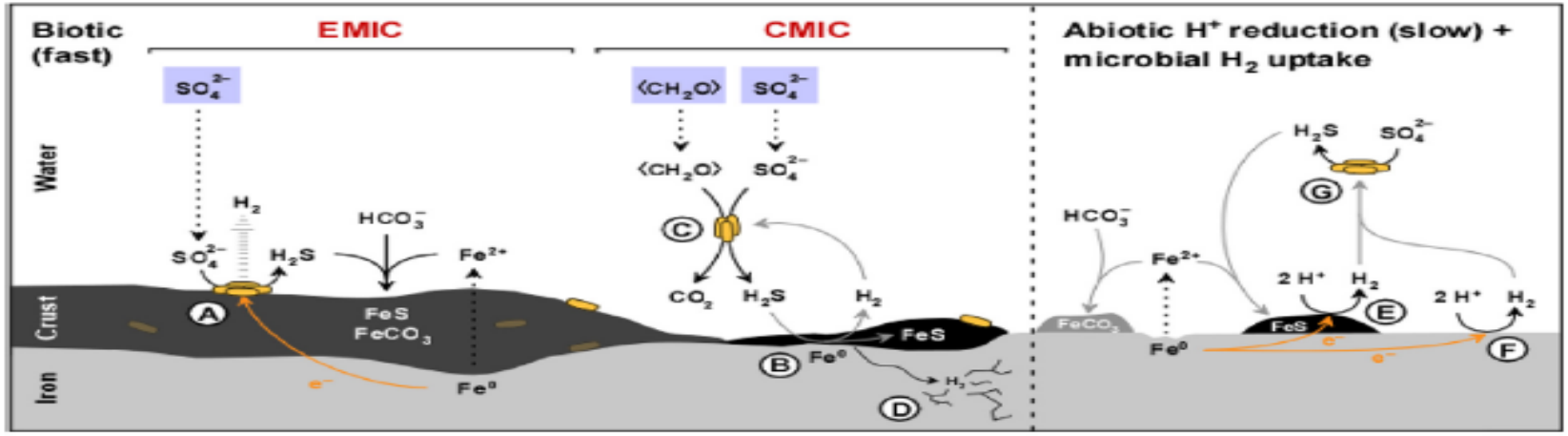
Starvation triggers pilus formation for better DET to harvest more electrons.



Sherar et al. Corrosion Sci, 53:955–960, 2011

Currently DET is still disputable. Cogent and direct evidence is needed to prove the occurrence of DET.

3. MIC classification



Stoichiometry of corrosive reactions

Electrical Microbially Influenced Corrosion (EMIC):

(A) $4\,Fe^0 + SO_4^{2-} + 3\,HCO_3^- + 5\,H^+ \rightarrow FeS + 3\,FeCO_3 + 4\,H_2O$

Chemical Microbially Influenced Corrosion (CMIC):

(B) $H_2S + Fe^0 \rightarrow H_2 + FeS$

(C) $3\langle CH_2O\rangle + 2\,Fe^0 + 2\,SO_4^{2-} + H^+ \rightarrow 3\,HCO_3^- + 2\,FeS + 2\,H_2O$

Sulfide Stress Cracking (SSC):

(D) $2\,H_{abs} \rightarrow H_2$

Abiotic:

(E) $Fe^0 + 2\,H^+ \xrightarrow{FeS} Fe^{2+} + H_2$

(F) $Fe^0 + 2\,H^+ \rightarrow Fe^{2+} + H_2$

(G) Same as (A), but slower

Major drawbacks:

(1) We demonstrated that MET of EET played a key role in MIC due to SRB. We further confirmed MET in MIC from genetic level (data unpublished).

(2) H_2S corrosion was not a sole chemical corrosion phenomenon.

1. Corrosion 70, 4, pp. 351-365, 2014.
2. Corrosion 71, 3, pp. 316-325, 2015.
3. Corrosion 71, 8, pp. 945-960, 2015.
4. Corrosion 70, 4, pp. 375-389, 2014.

3. MIC classification

EET - MIC (electroactive or electrogenic biofilm)

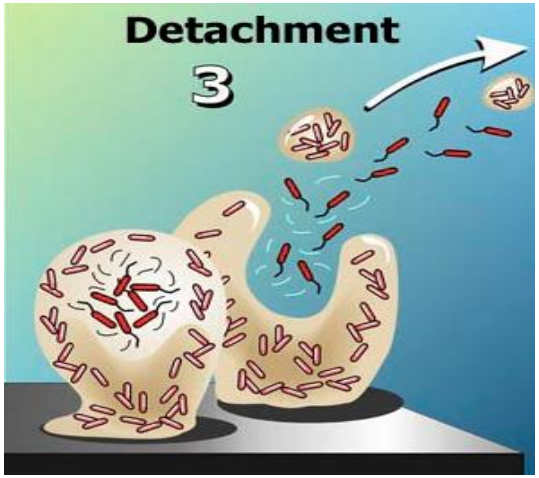
Biofilms rely on anaerobic respiration for energy. Oxidant (e.g., sulfate and nitrate) is reduced inside cells under biocatalysis. SRB, NRB, methanogens, etc. intentionally cause corrosion for energy.

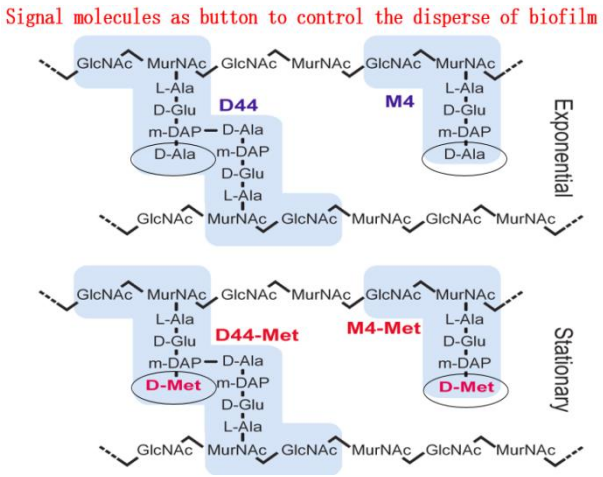
Metabolites - MIC

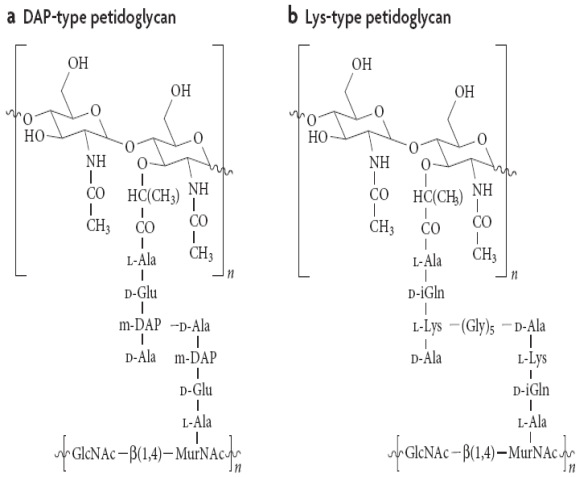
Fermentative bacteria and fungi in biofilms secrete organic acids. The produced oxidants (organic acids, H^+, etc.) in MIC are reduced outside cells without biocatalysis.

May or may not be intentional. These oxidants will corrode in conventional chemical corrosion (such as acetic acid corrosion) without biofilms! APB (and some SRB and NRB) that perform anaerobic fermentation cause this type of MIC.

4. D-amino acids as biocide enhancer







Biotechnology Advances 31 (2013) 1738–1753

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

Research review paper

Current and emerging environmentally-friendly systems for fouling control in the marine environment

Jeanette E. Gittens [a], Thomas J. Smith [a,*], Rami Suleiman [b], Robert Akid [c]

D-Amino acids have been found to disrupt bacterial biofilms and are promising components for novel antifouling systems. In experiments by Xu et al. (2012), a combination of D-tyrosine and the "green" biocide tetrakis hydroxymethyl phosphonium sulfate (THPS) has been found to inhibit formation of biofilms of the corrosion-causing SRB *Desulfovibrio vulgaris* in laboratory tests on carbon steel surfaces over a period of seven days. Results showed that at a concentration of only 1 ppm, D-tyrosine was able to reduce the amount of THPS required to kill the SRB biofilm from 100 to 50 ppm (Xu et al., 2012).

Tingyue Gu, Dake Xu, Compositions and Methods for treating biofilms. PCT Patent Application No. PCT/US12/52417. Patent WO2013032961A1

Advantages of D-amino acids as biocide enhancer

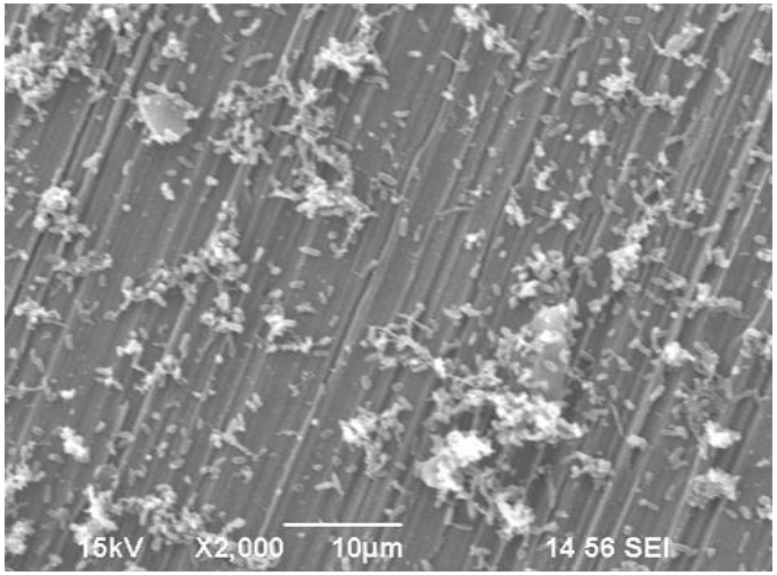
1. Broad-spectrum signal molecular
2. Low toxicity
3. Biodegradable
4. Low price

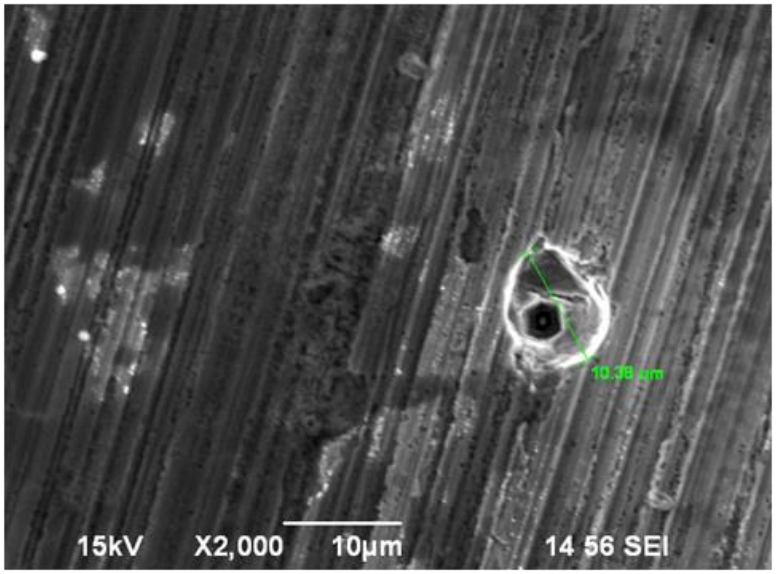
Microbiologically Influenced Corrosion (MIC) Resistance of a Novel Cu-bearing 2205 Duplex Stainless Steel in the Presence of a Marine *Pseudomonas aeruginosa* Biofilm

Work done@IMR

MIC background

- MIC corrodes carbon steel.
- MIC attacks 304/304L SS, 316/316L SS, 2205 DSS and 2707 HDSS.
- MIC even attacks Copper and Ti.

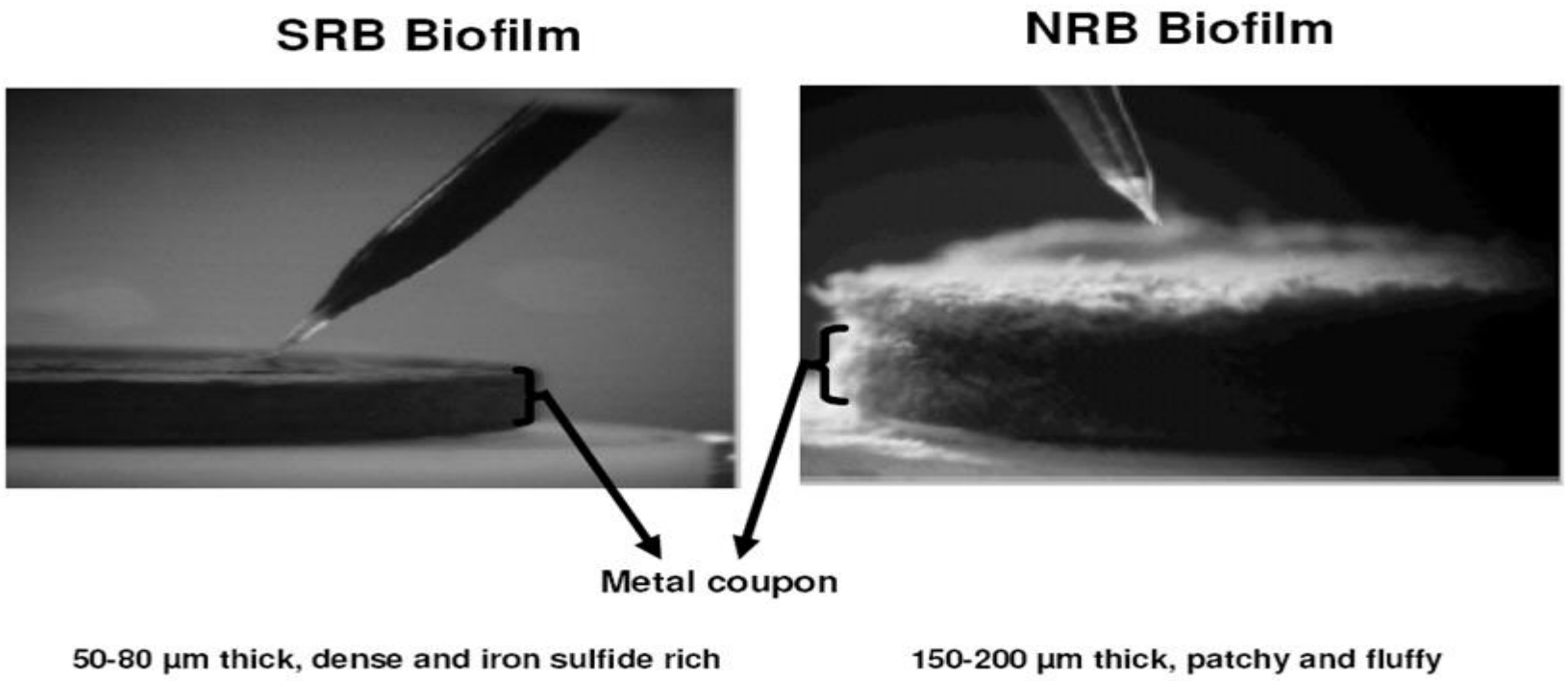




316L pitting corrosion due to SRB after coculture for 7 days

MIC background

Biofilms are responsible for MIC



It is widely accepted that MIC related pitting corrosion is caused by the biofilm. So if the biofilm can be effectively inhibited or mitigated, the occurrence of pitting corrosion due to MIC can be considerably decreased.

Larson et al., NACE Paper 07507, 2007

Mitigation of MIC

Current Mitigation Methods

- **Biocides/Biostats (THPS and glutaraldehyde, etc.)**

Problems with toxicity, resistance, high costs, strict environmental regulations.

- **Physical scrubbing (pigging)**

Some pipelines cannot be pigged.

- **Microbial competition**

NRB can be used to mitigate souring, but not necessarily MIC. Because they are corrosive bugs!

In USA, $1.2 billon was spent annually on biocide to fight MIC.

Aim to eradicate biofilm (planktonic cells are much easier to be killed). Biofilms are far more difficult to eradicate than planktonic cells. 10X or higher doses. 1,000X reported.

Innovative MIC mitigation method from material aspect

Antibacterial Stainless Steels

Copper ions show strong antibacterial ability, and copper is a vital alloy element. Based on this, adding suitable quantity of copper is the technical approach to develop antibacterial stainless steel.

IMR developed various types of stainless steel, including austenitic antibacterial SS (304-Cu, 316L-Cu, 317L-Cu, 201-Cu), ferritic antibacterial SS (430-Cu) and martensitic antibacterial SS (420-Cu, 2Cr13Mo-Cu,17-4PH Cu).

A newly developed 2205-Cu duplex SS was aimed to mitigate the MIC due to corrosive microbes in marine environments.

Antibacterial stainless steel

Broad antibacterial spectrum

Experimental bacteria	Antibacterial rate（%）		
	Ferritic antibacterial stainless steel	Austenitic antibacterial stainless steel	Contrast steel
Escherichia coli ATCC25922	99.9	99.9	0
Shigella fexneri ATCC12022	99.0	99.5	0
Pseudomonas aeruginosa ATCC9721	99.9	99.9	0

Antibacterial spectrum of the antibacterial stainless steels against the gram-negative bacteria.

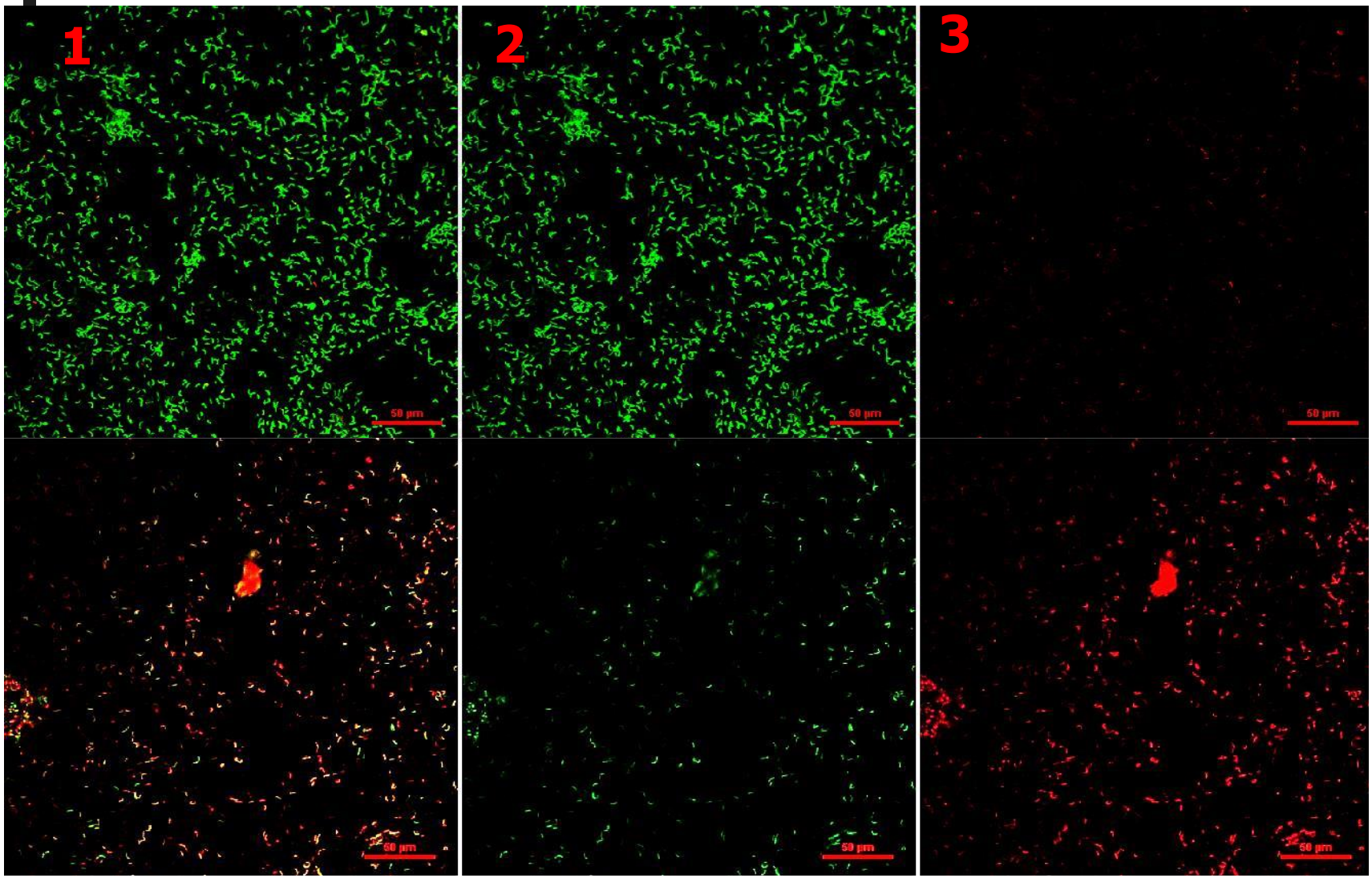
Antibacterial stainless steel

Broad antibacterial spectrum

Experimental bacteria	Antibacterial rate（%）		
	Ferritic antibacterial stainless steel	Austenitic antibacterial stainless steel	Contrast steel
Staphylococcus epidermis ATCC14990	99.9	99.9	0
Sarcina lutea ATCC9341-A	99.9	99.9	0
Serratia marcescens ATCC8100	98.2	99.5	0
Bacillus pumilus ATCC14884	97.7	92.4	0
Enterococcus faecalis ATCC29212	91.0	93.6	0

Antibacterial spectrum of the antibacterial stainless steels against the gram-positive bacteria.

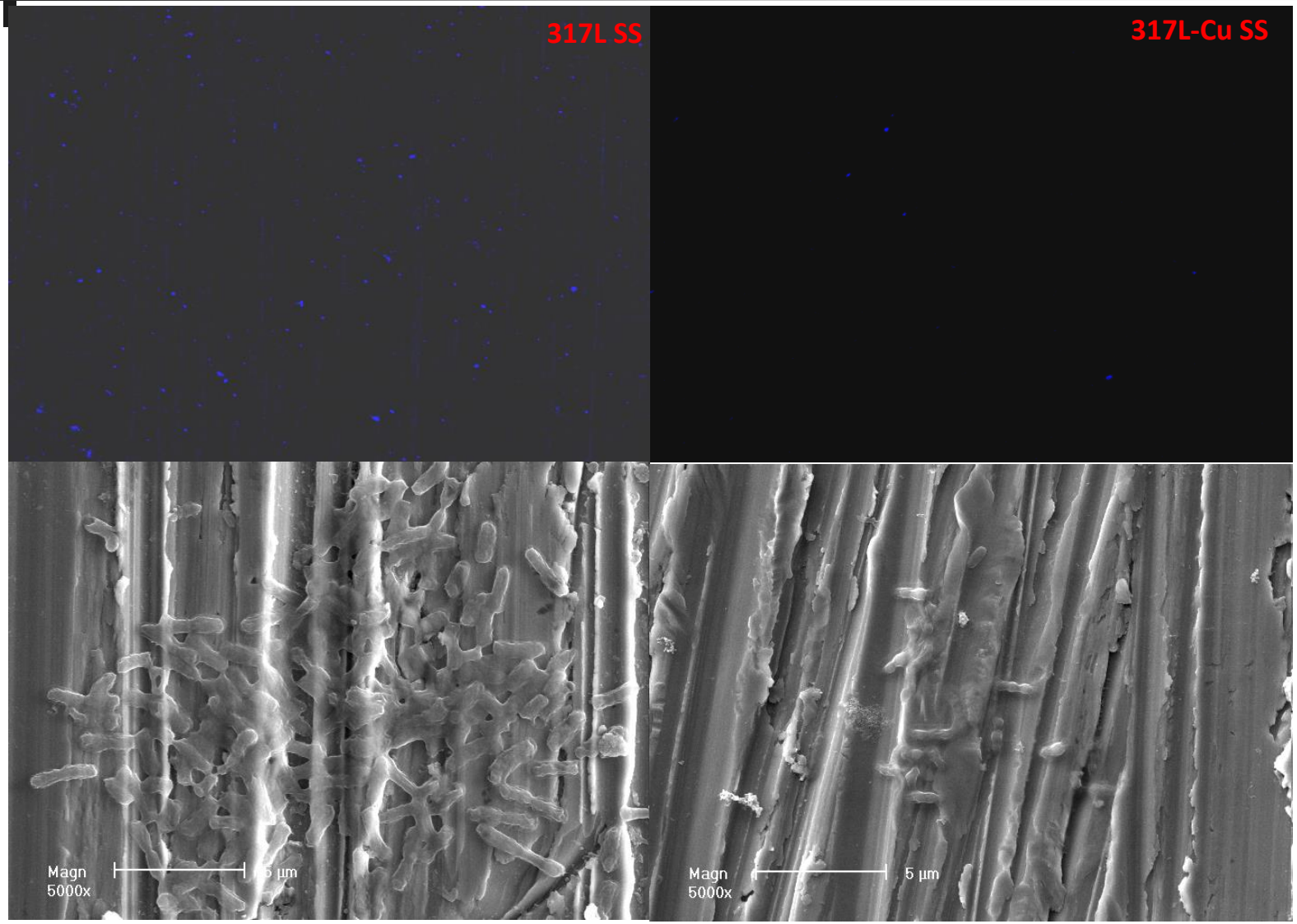
Antibacterial stainless steel



Tap water exposed in air after 24h, (A) 304 SS, (B) 304–Cu,

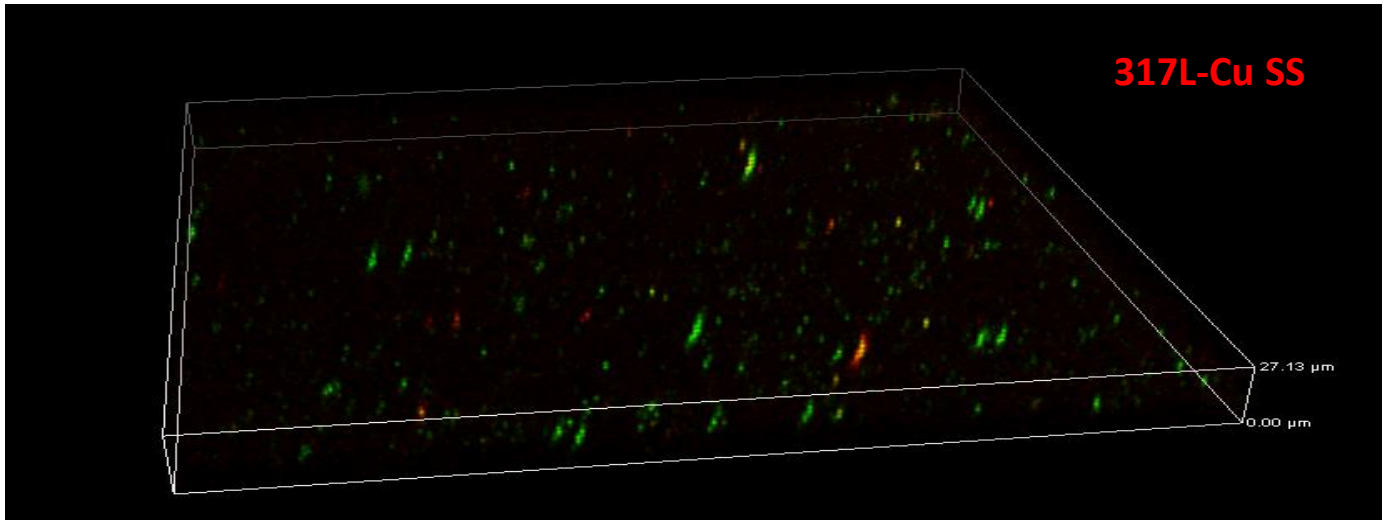
1-Live/Dead staining, 2-Live sessile cells, and 3-Dead sessile cells.

Antibacterial stainless steel

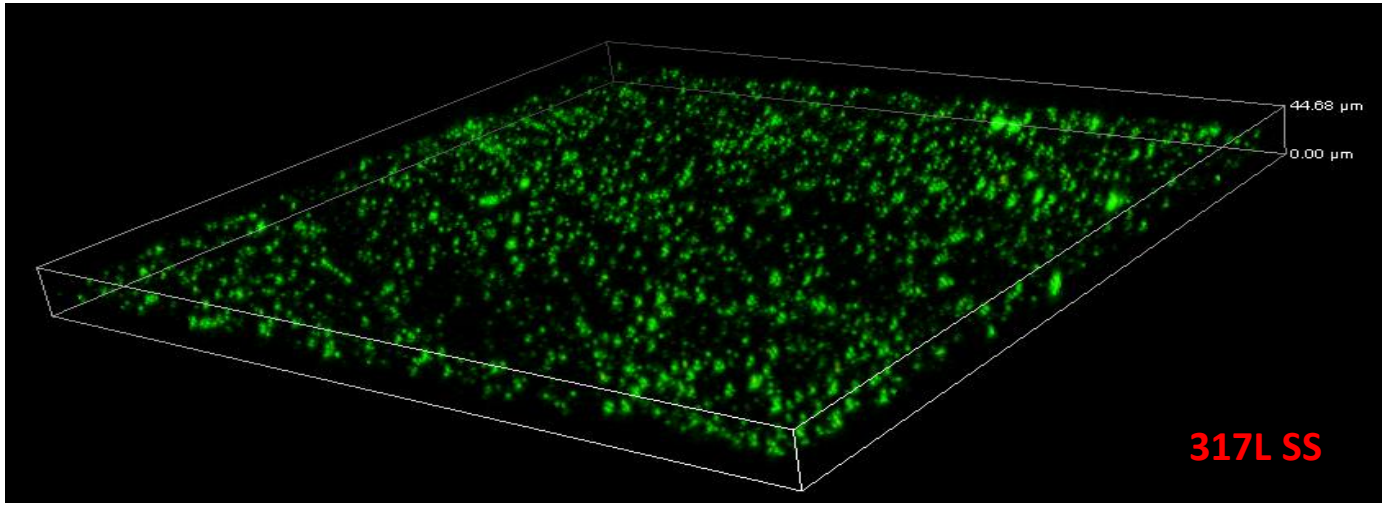


Cultured in 0.9% NaCl solution for 24h

Antibacterial stainless steel



Maximal biofilm thickness: **27.43 µm**



Maximal biofilm thickness: **44.68 µm**

Cultured in 0.9% NaCl solution for 24h in presence of *E. coli*

Antibacterial stainless steel

MIC resistance test of 304-Cu against *Escherichia coli*

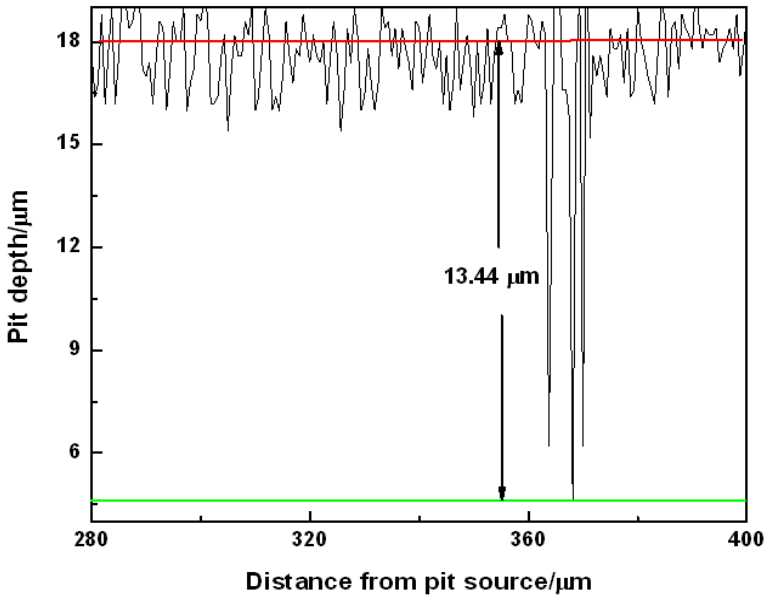
Electrochemical parameters for stainless steel specimens exposed to LB medium with and without *E.coli.*

Specimen	Solutions	Time (day)	E_{corr} (mV)	E_{pit} (mV)	I_{corr} (μA/cm²)
304 SS	LB	2	-131	332	0.03
		21	-131	325	0.19
	LB+bacteria	2	-286	221	1.42
		21	-519	-369	4.98
304-Cu SS	LB	2	-186	161	0.03
		21	-187	168	0.07
	LB+bacteria	2	-192	264	0.08
		21	-324	-174	1.24

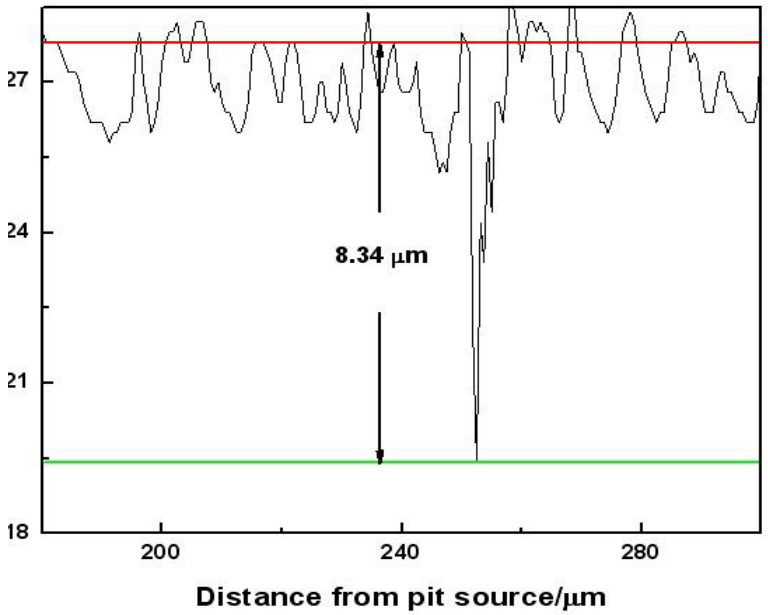
Antibacterial stainless steel

Corrosion characteristics of stainless steels exposed to LB medium with *E. coli* for 21 days.

Specimen	Maximum pit depth (μm)	Pitting rate* (mm/year)	R_a (μm)	Weight loss (mg/cm^2)
304 SS	13.4	0.23	1.17±0.03	0.6±0.05
304-Cu SS	8.3	0.14	0.65±0.02	0.2±0.03



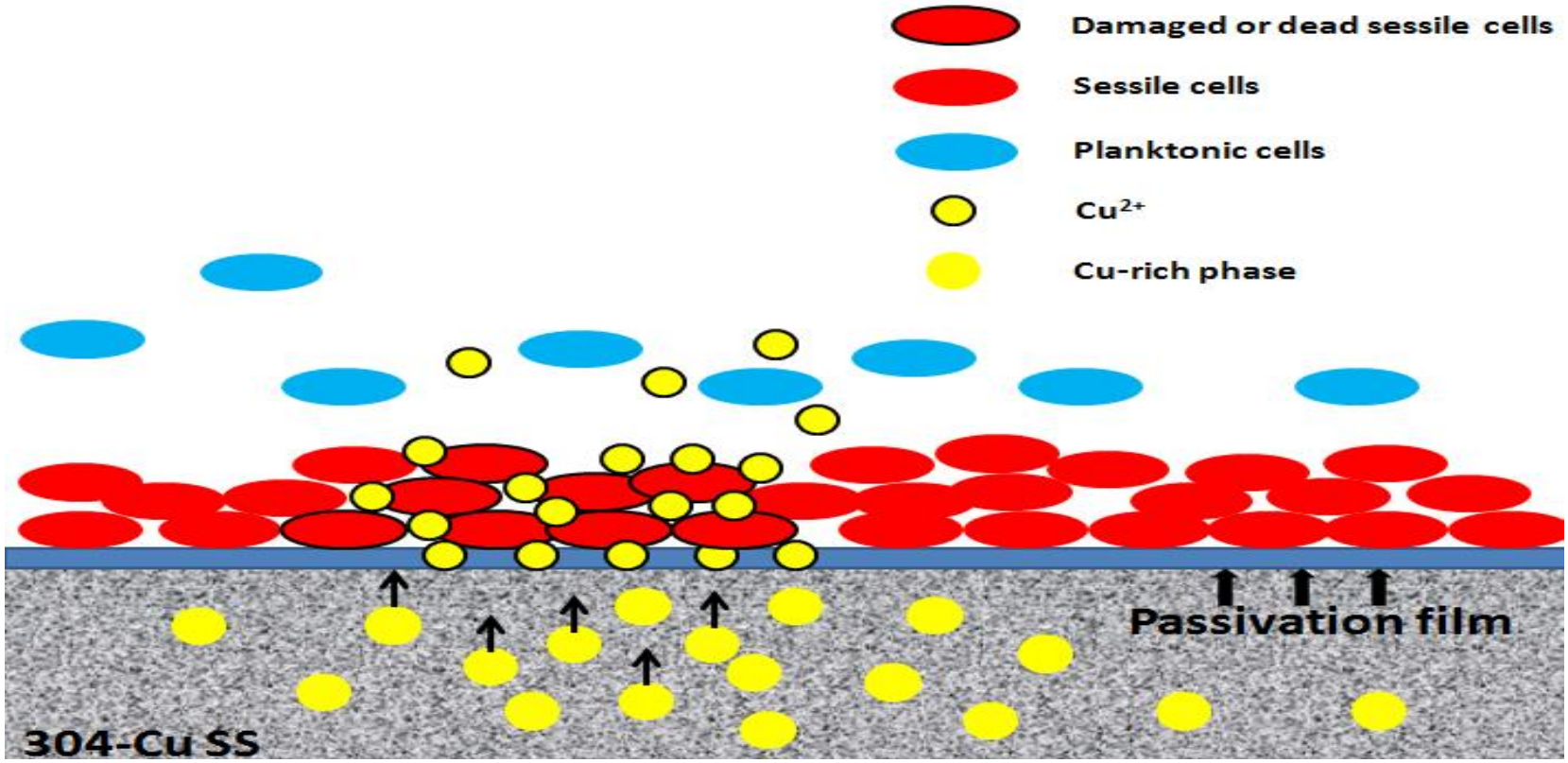
304 SS



304-Cu SS

Antibacterial stainless steel

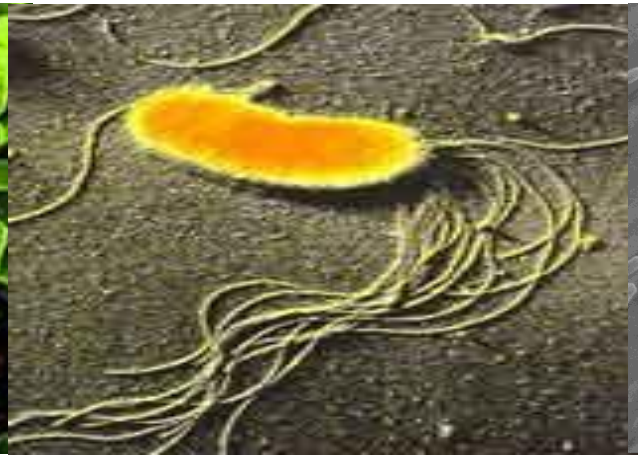
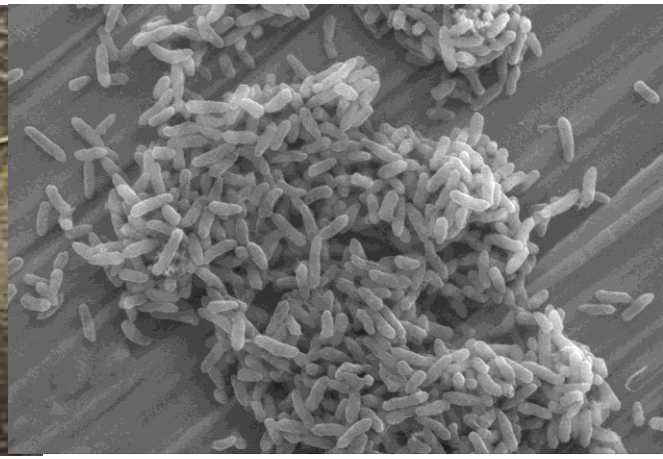
Summary:
Unlike traditional mitigation methods, the innovative idea of this research is to utilize the antibacterial stainless steel surface (the Cu-rich phase and the Cu ions released from the matrix) where the biofilm attached to directly mitigate the corrosive biofilm.



2205-Cu DSS mitigated MIC

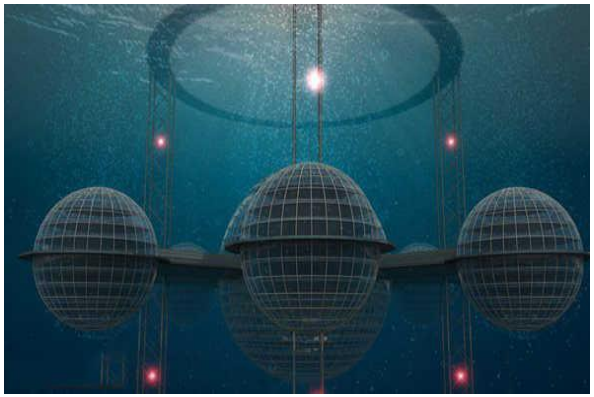
- ***Pseudomonas aeruginosa*** **is a Gram-negative motile rod bacterium widely distributed in nature.**
- ***P. aeruginosa*** **is an aerobic marine corrosive microbe, which have caused many MIC cases.**
- **It has been recognized as the pioneer colonizer in the process of biofilm formation.**

Biofilm formation + Corrosive

2205 DSS

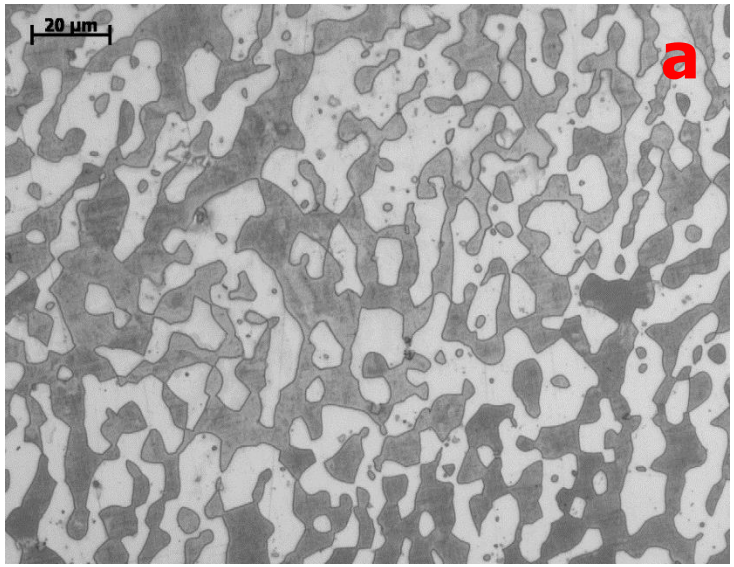
2205 DSS has been widely used in the marine environments, such as ships, offshore platform, subsea equipment, coastal facility and the use of seawater cooling equipment.

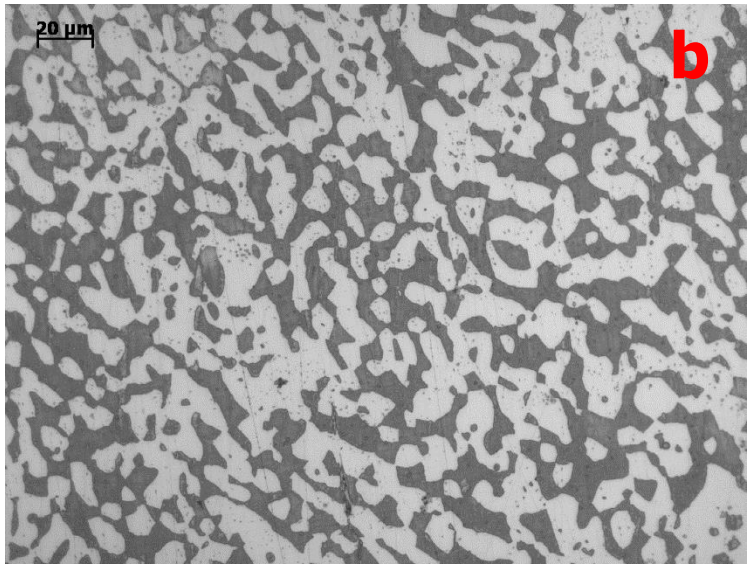


2205-Cu DSS mitigated MIC

Antibacterial Stainless Steel used in marine environment

2205 duplex SS is widely used in marine environments. In recent, the failures of 2205 DSS due to MIC were reported. The MIC resistance of a novel Cu-bearing 2205 Duplex Stainless Steel (2205 Cu-DSS) against an aerobic marine *P. aeruginosa* biofilm was investigated.





Microstructure of 2205 Cu-DSS after
(a) solution at 1050°C.
(b) solution at 1050°C, and aging at 540°C for 4 h.

2205-Cu DSS mitigated MIC

Mechanical properties

Samples	δ_s (MPa)	δ_b (MPa)	σ (%)	ψ (%)	H (Hv)
a	540	770	76	38	380
b	636	886	74	32	471
c	571	810	77	30	369

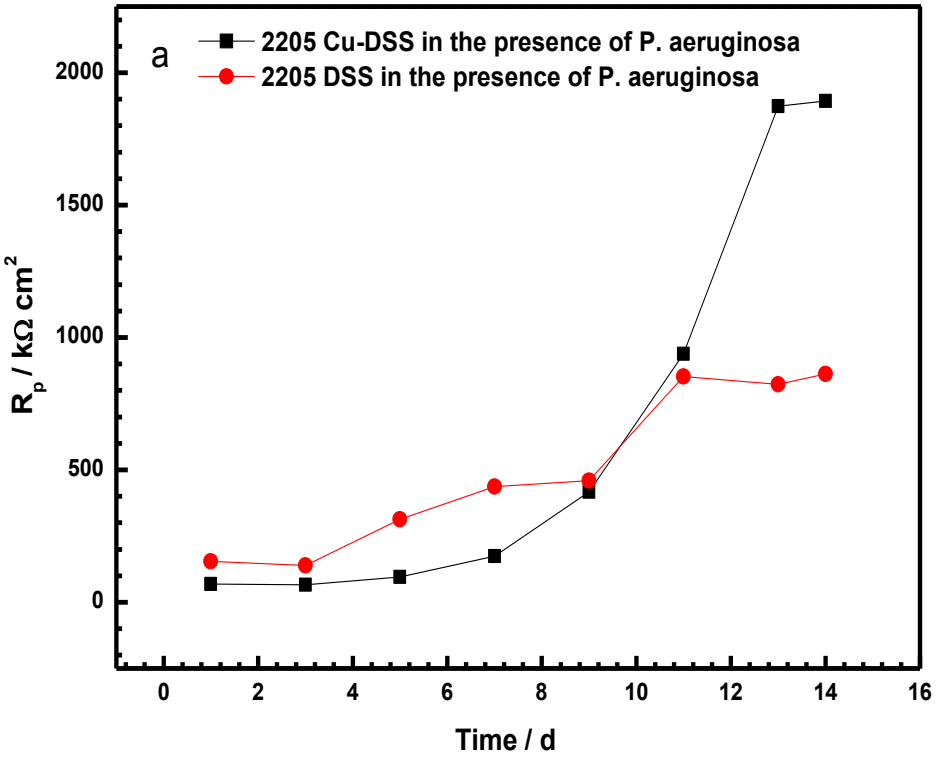
Where δ_s is the yield strength, δ_b tensile strength, σ elongation, ψ cross sectional area and hardness H.

a. commercial 2205 DSS
b. 2205 Cu-DSS after solution and aging treatment
c. 2205 Cu-DSS after solution treatment

The mechanical properties of 2205-Cu were slightly better than those of the commercial 2205.

2205-Cu DSS mitigated MIC

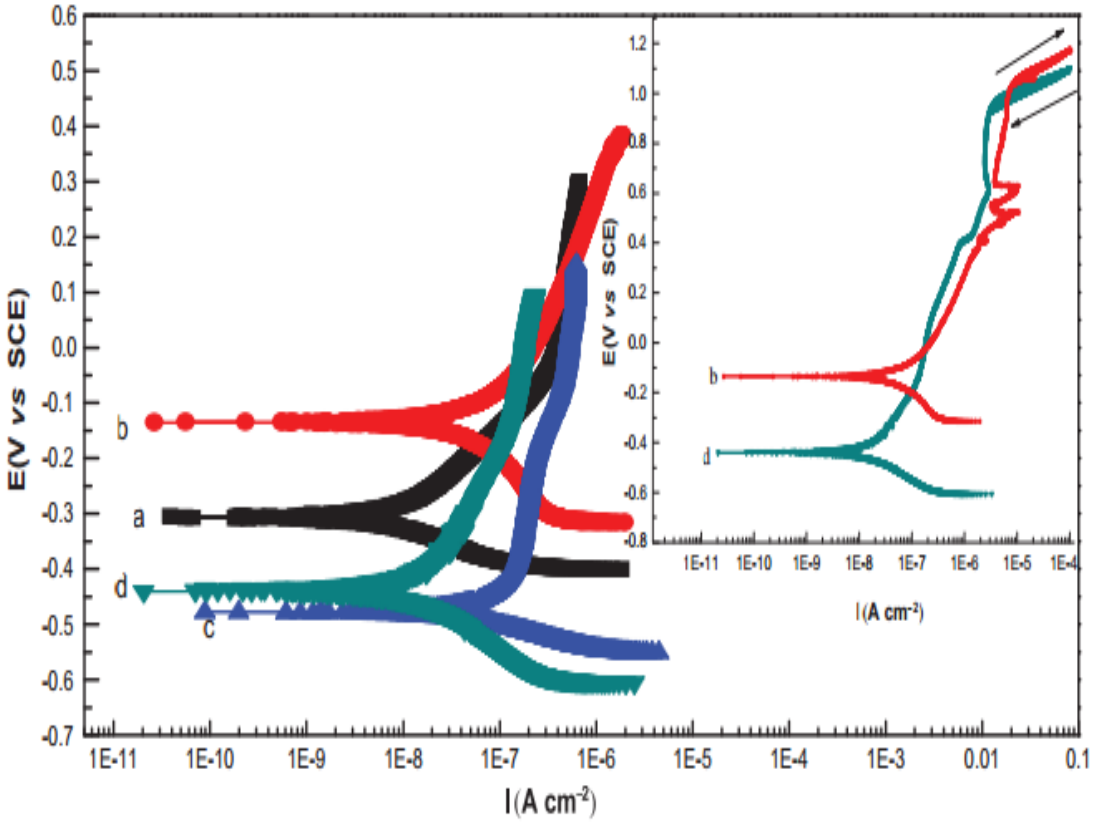
MIC resistance test – Linear polarization resistance



The variations of *R*p with exposure time for 2205 DSS and 2205 Cu-DSS coupons in the presence of *P. aeruginosa* at 30℃.

The R_p of 2205-Cu was larger than that of the commercial 2205, indicating its better MIC resistance against *P. aeruginosa*.

2205-Cu DSS mitigated MIC



(a) 2205 DSS in the uninoculated medium

(b) 2205 DSS in the medium inoculated with *P. aeruginosa*

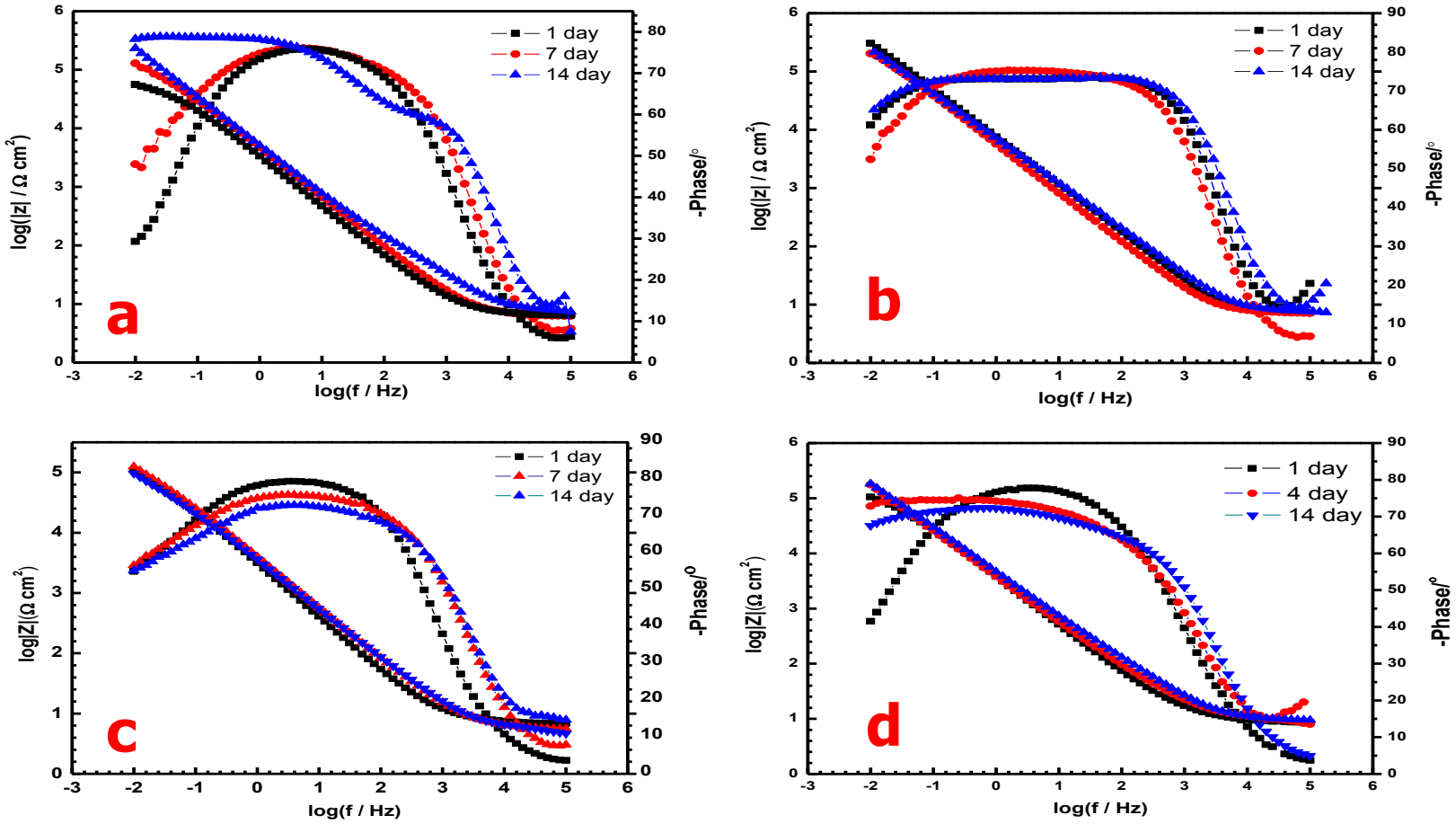
(c) 2205 Cu-DSS in the uninoculated medium

(d) 2205 Cu-DSS in the medium inoculated with *P. aeruginosa* after 14 days of incubation

	Sterile medium		After inoculation	
	2205 DSS	2205 Cu-DSS	2205 DSS	2205 Cu-DSS
E_{corr} / mV (Vs. SCE)	-308.2	-478.5	-135.2	-437.1
i_{corr} / (μA cm^2)	0.01	0.13	0.20	0.04
β_a (V / dec)	0.18	0.99	0.56	0.62
β_c (V / dec)	-0.09	-0.08	-0.58	-0.20

2205-Cu DSS mitigated MIC

MIC resistance test – Electrochemical Impedance Spectroscopy

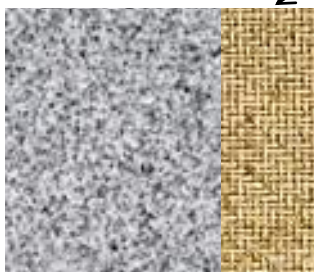


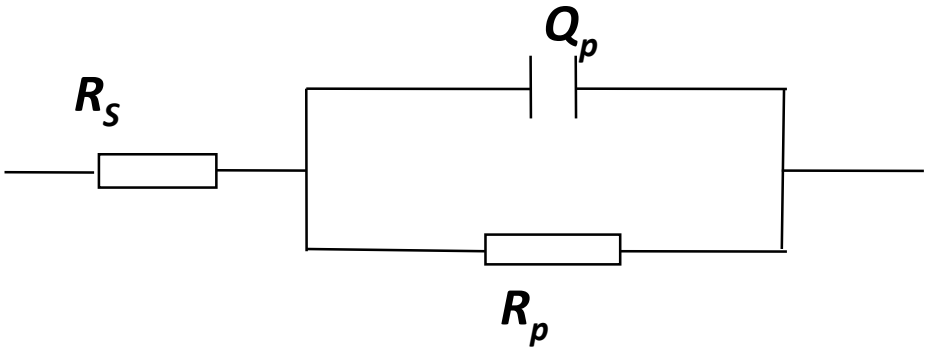
The Bode plots of 2205 DSS and 2205 Cu-DSS coupons with or without exposure to *P. aeruginosa* biofilm: (a) 2205 Cu-DSS in the medium inoculated with *P. aeruginosa*, (b) 2205 DSS in the medium inoculated with *P. aeruginosa*, (c) 2205 DSS in the uninoculated medium, and (d) 2205 Cu-DSS in the uninoculated medium.

2205-Cu DSS mitigated MIC

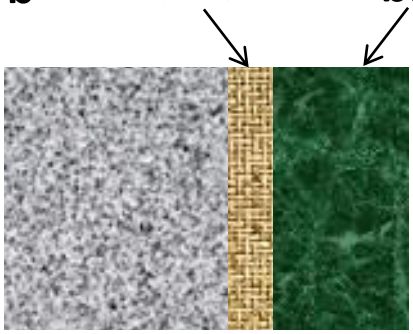
MIC resistance test – The equivalent physical models and the corresponding circuit models

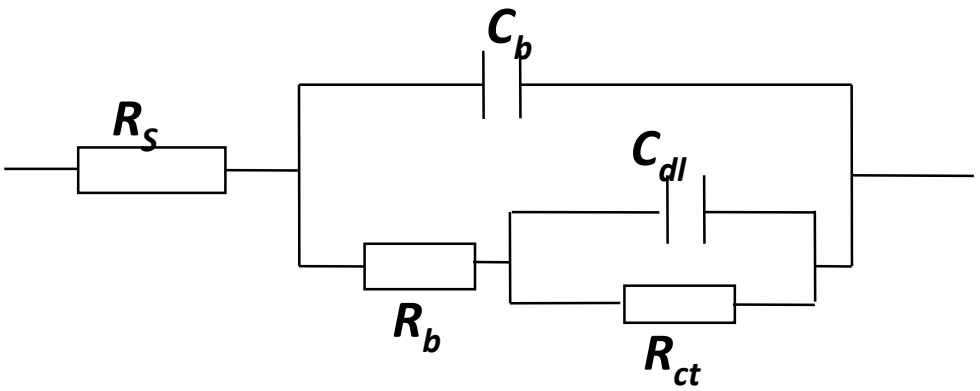
a Passive film





b Passive film biofilm





(a) a single, and (b) a double layer model with a biofilm.

2205-Cu DSS mitigated MIC

MIC resistance test – The efficiency of MIC resistance

Day	11	13	14
η_p%	n/a	n/a	89
η_R%	57	81	88

$$\eta_p = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \times 100\%$$

$$\eta_R = \frac{R_{ct(inh)} - R_{ct(uninh)}}{R_{ct(inh)}} \times 100\%$$

The inhibition efficiency of 2205 Cu-DSS in the presence of *P. aeruginosa*.

η_p was calculated by the i_{corr} of 2205-Cu DSS vs. the i_{corr} of 2205 DSS in the presence of *P. aeruginosa*.

η_R was calculated by the R_{ct} of 2205-Cu DSS vs. the R_{ct} of 2205 DSS in the presence of *P. aeruginosa*.

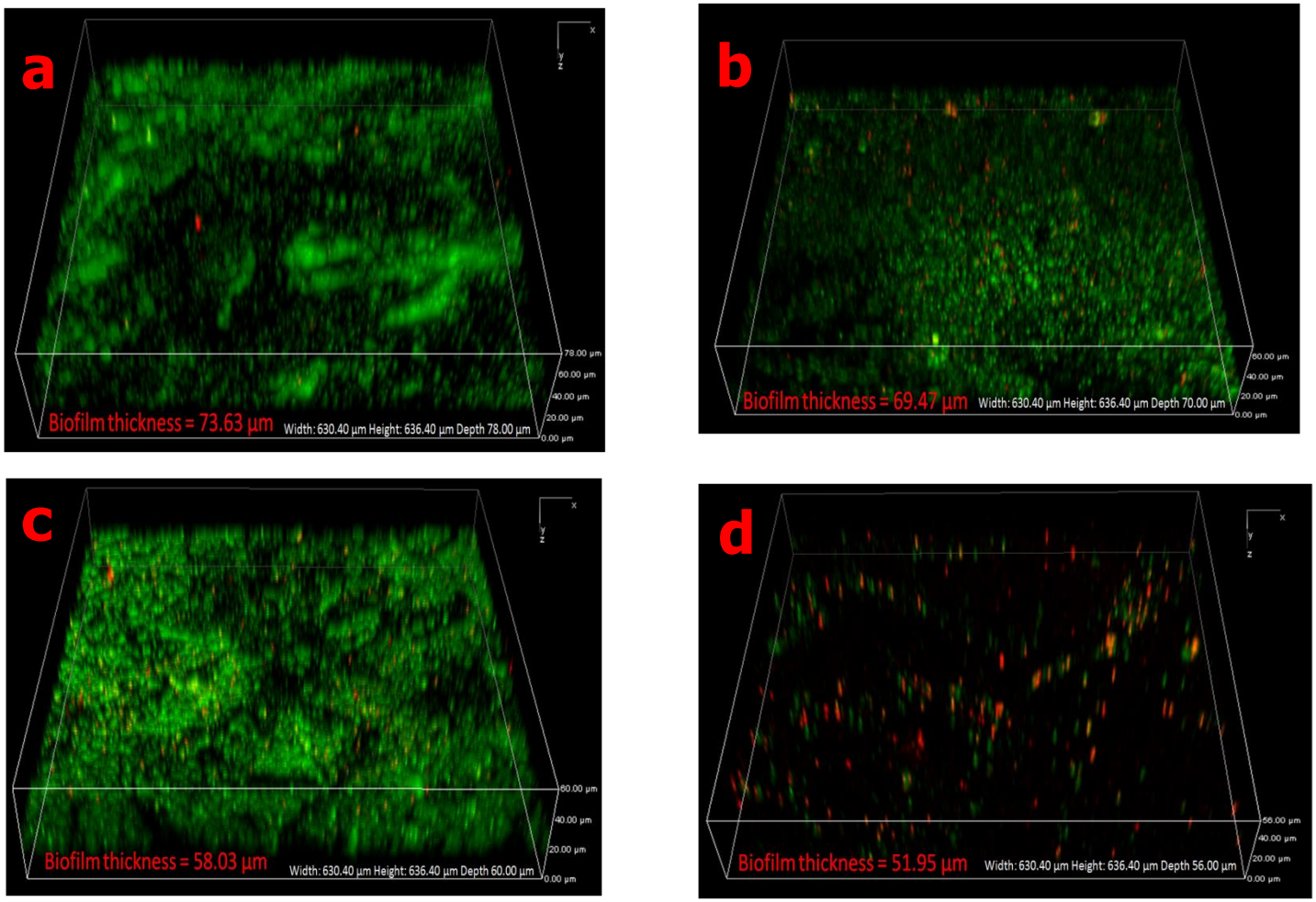
$i_{corr(uninh)}$ and $R_{ct(uninh)}$
2205 DSS+ *P. aeruginosa*

$i_{corr(inh)}$ and $R_{ct(inh)}$
2205-Cu DSS + *P. aeruginosa*

The η_p and η_R demonstrate that the 2205-Cu DSS showed its MIC resistance against *P . aeruginosa* after 11 days.

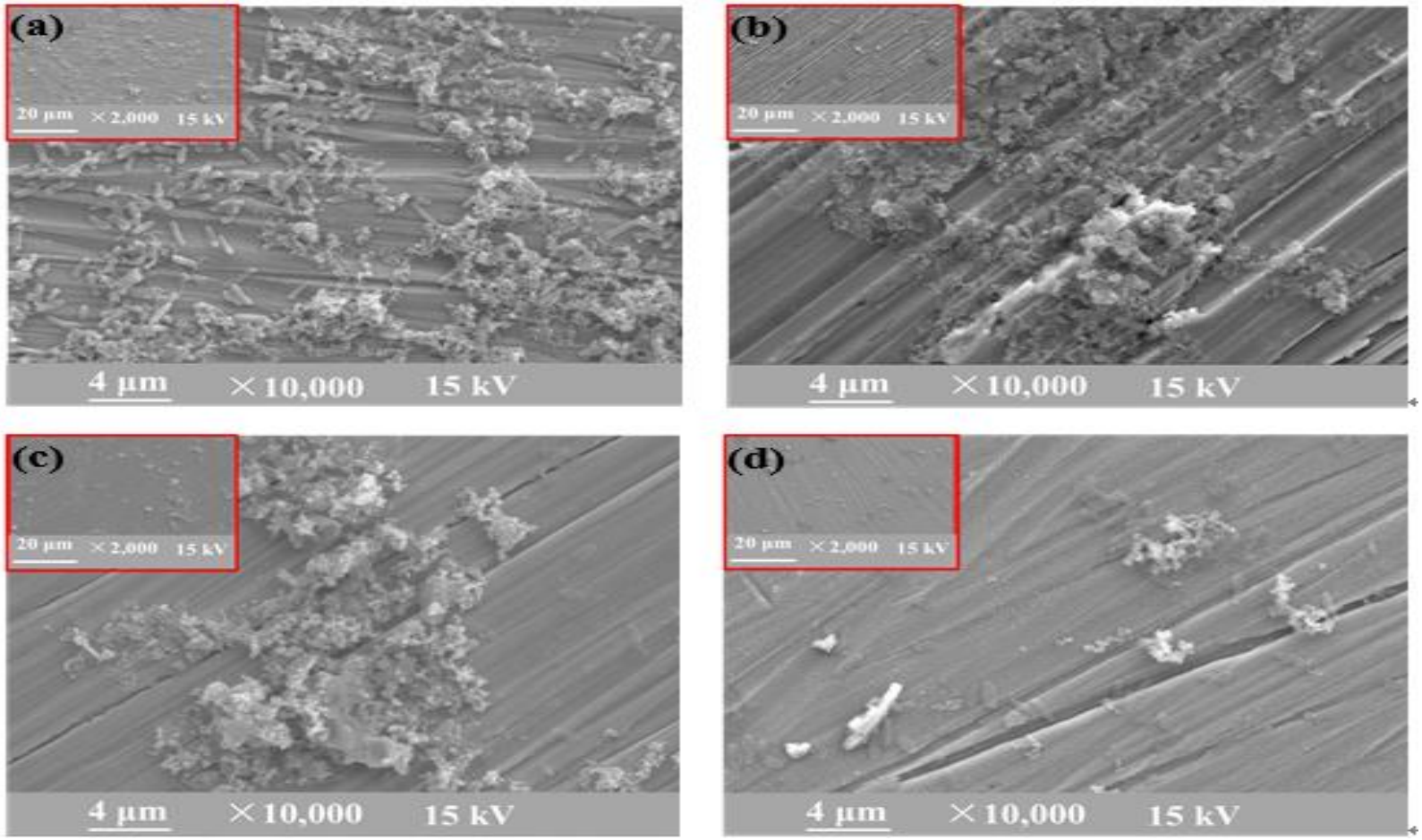
2205-Cu DSS mitigated MIC

MIC resistance test – Live/Dead staining



CLSM to investigate the growth of the *P. aeruginosa* biofilm on the surface of: (a) 2205 DSS after 1 day, (b) 2205 Cu-DSS after 1 day, (c) 2205 DSS after 7 days, and (d) 2205 Cu-DSS after 7 days.

2205-Cu DSS mitigated MIC

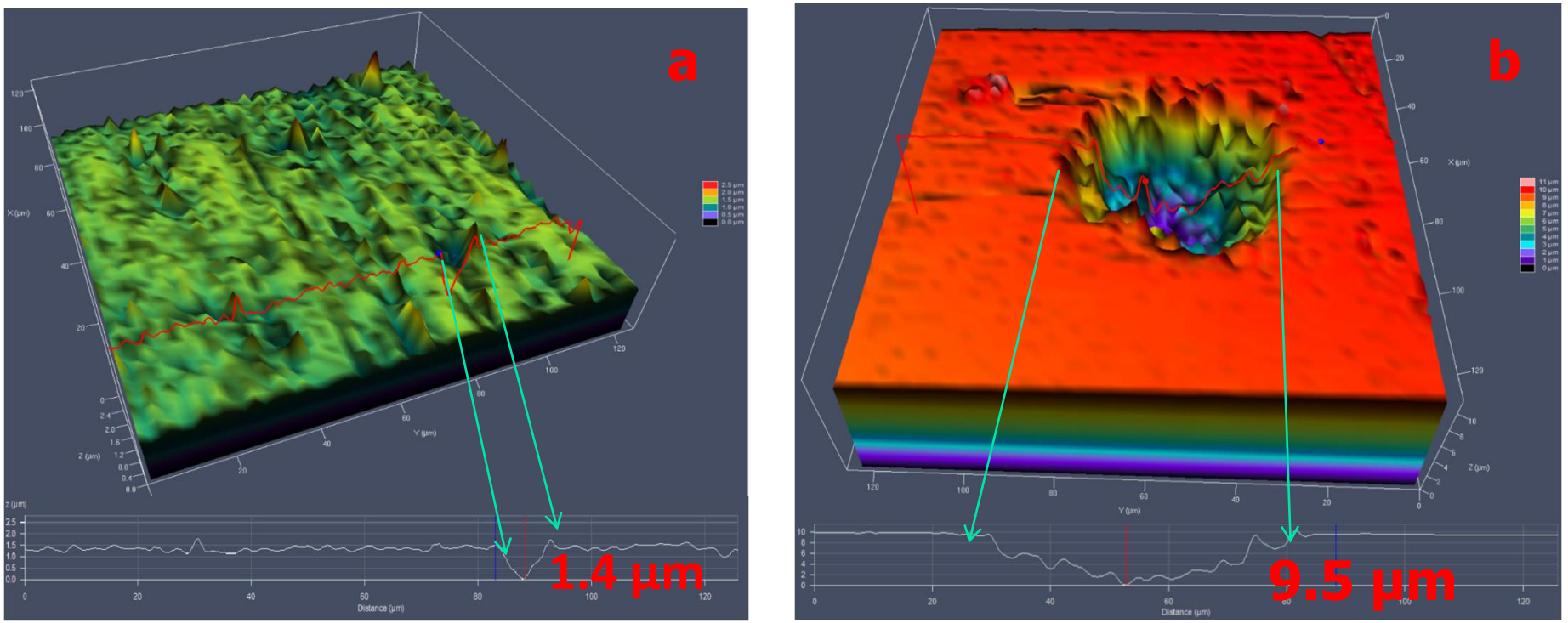


(a) 2205 DSS in the presence of *P. aeruginosa* after 7 days, (b) 2205-Cu DSS in the presence of *P. aeruginosa* after 7 days, (c) 2205 DSS in the presence of *P. aeruginosa* after 14 days, and (d) 2205-Cu DSS in the presence of *P. aeruginosa* after 14 days.

The Live/Dead staining and SEM images confirmed the strong biofilm removal efficacy of 2205-Cu DSS compared with 2205 DSS.

2205-Cu DSS mitigated MIC

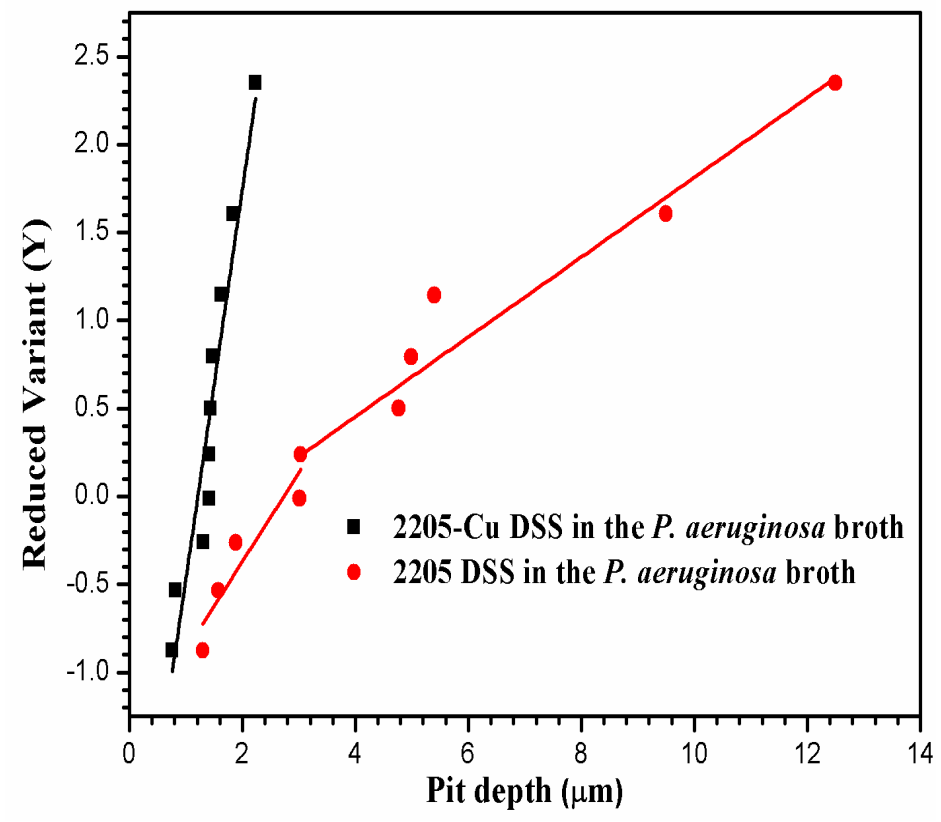
MIC resistance test – Surface morphology observation

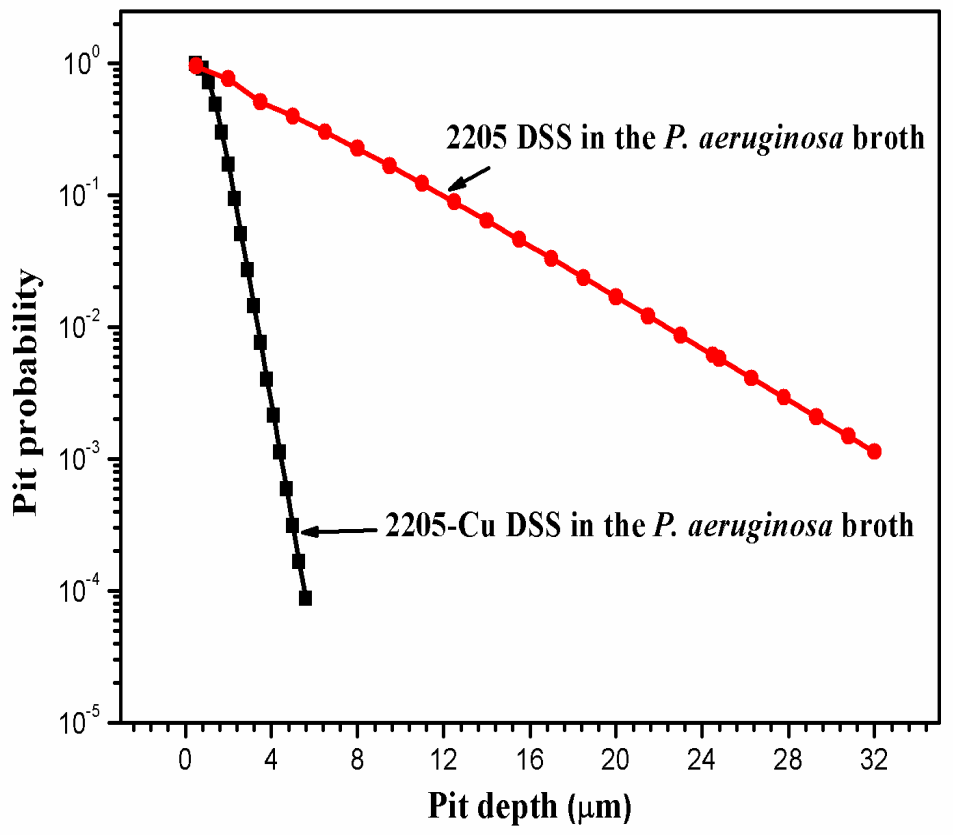


The CLSM 3-D images of (a) 2205 Cu-DSS and (b) 2205 DSS incubated in the medium inoculated with *P. aeruginosa* for 14 days.

The MIC resistance performance of 2205-Cu was supported by the pit depth data.

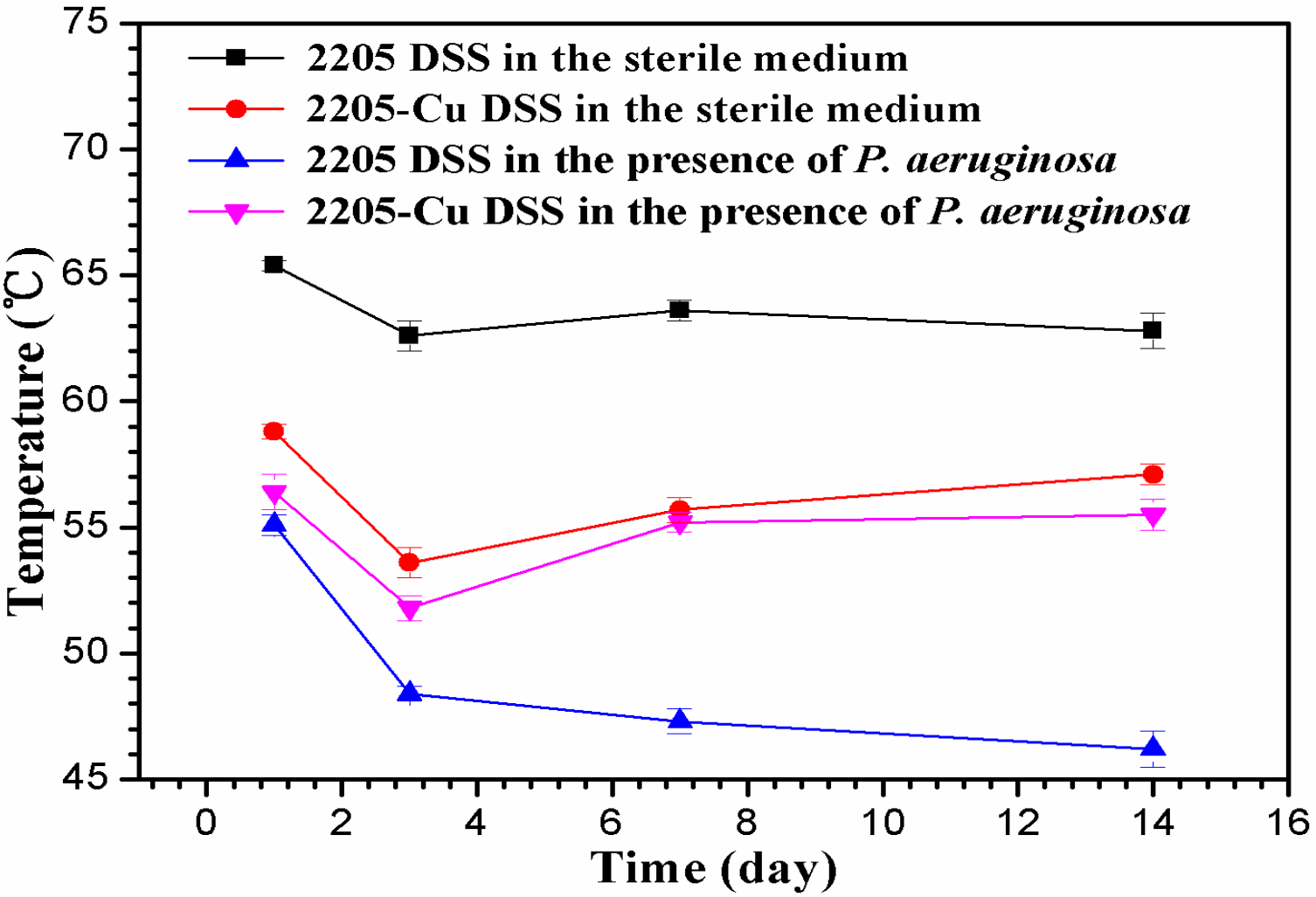
2205-Cu DSS mitigated corrosive biofilm





2205-Cu DSS possessed strong MIC pitting resistance.

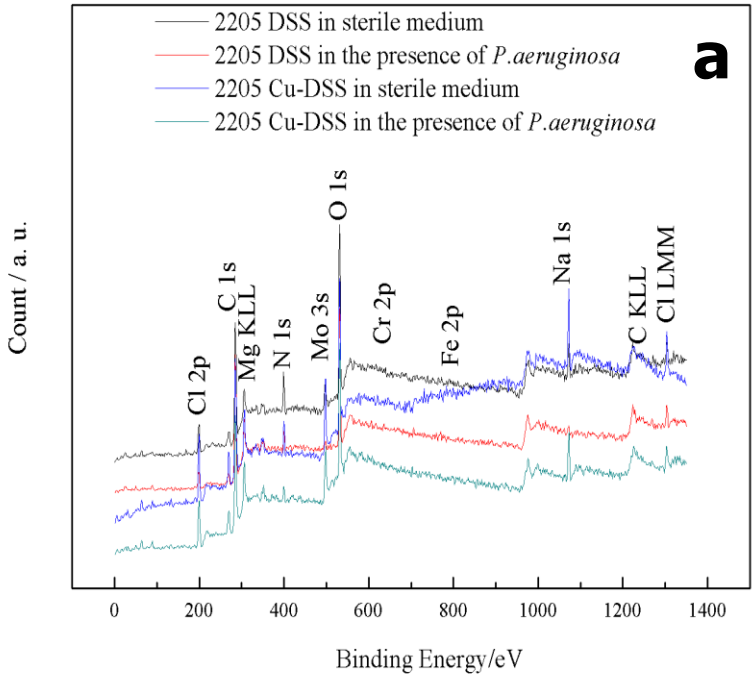
2205-Cu DSS mitigated corrosive biofilm

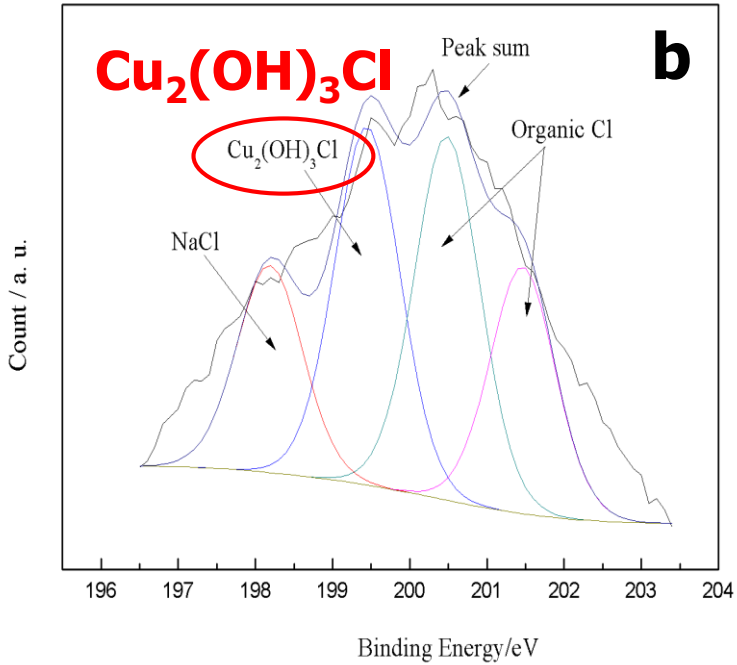


2205 Cu-DSS showed considerably larger CPT values, indicating its strong pitting resistance.

2205-Cu DSS mitigated MIC

MIC resistance test – Surface analysis



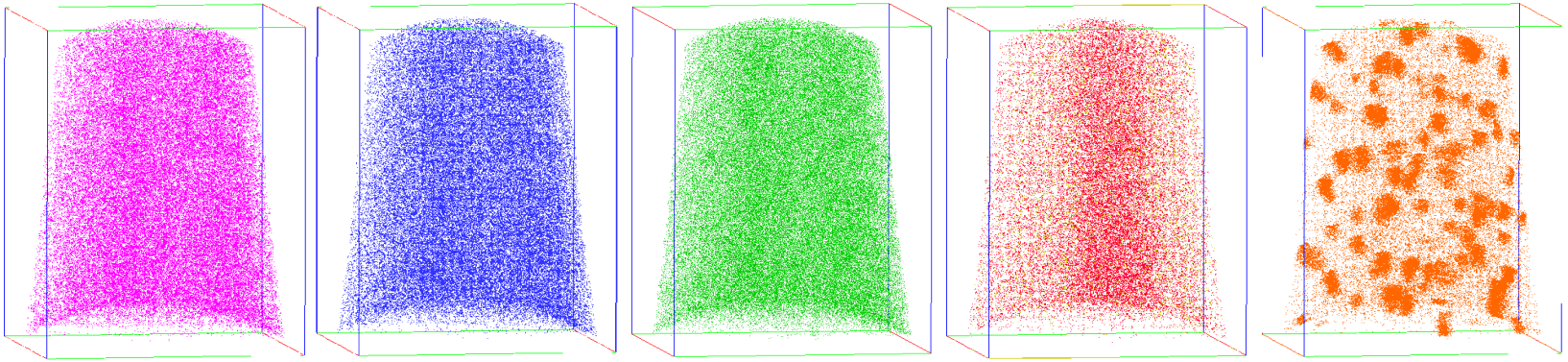


(a) The wide XPS spectra of the surface of the 2205 DSS and 2205 Cu-DSS in the medium with and without *P. aeruginosa* after 14 days of incubation,(b) the high resolution XPS spectra of Cl 2p for 2205 Cu-DSS with exposure to *P. aeruginosa* after 14 days of incubation, and (c) the high resolution XPS spectra of Cl 2p for 2205 DSS with exposure to *P. aeruginosa* after 14 days of incubation.

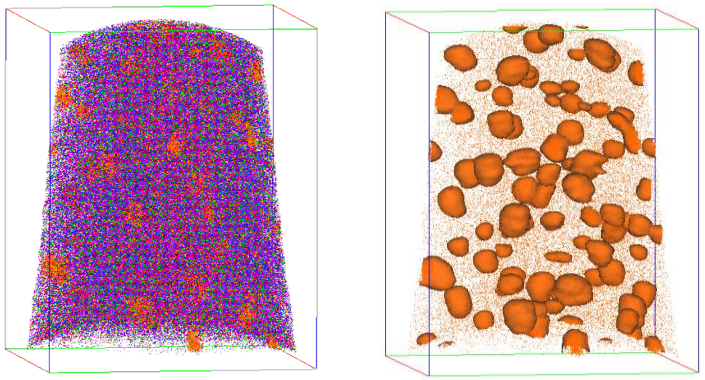
A protective $Cu_2(OH)_3Cl$ layer was formed on the 2205 Cu-DSS surface.

2205-Cu DSS mitigated MIC

3D atom probe



Fe Cr Ni Mo Cu



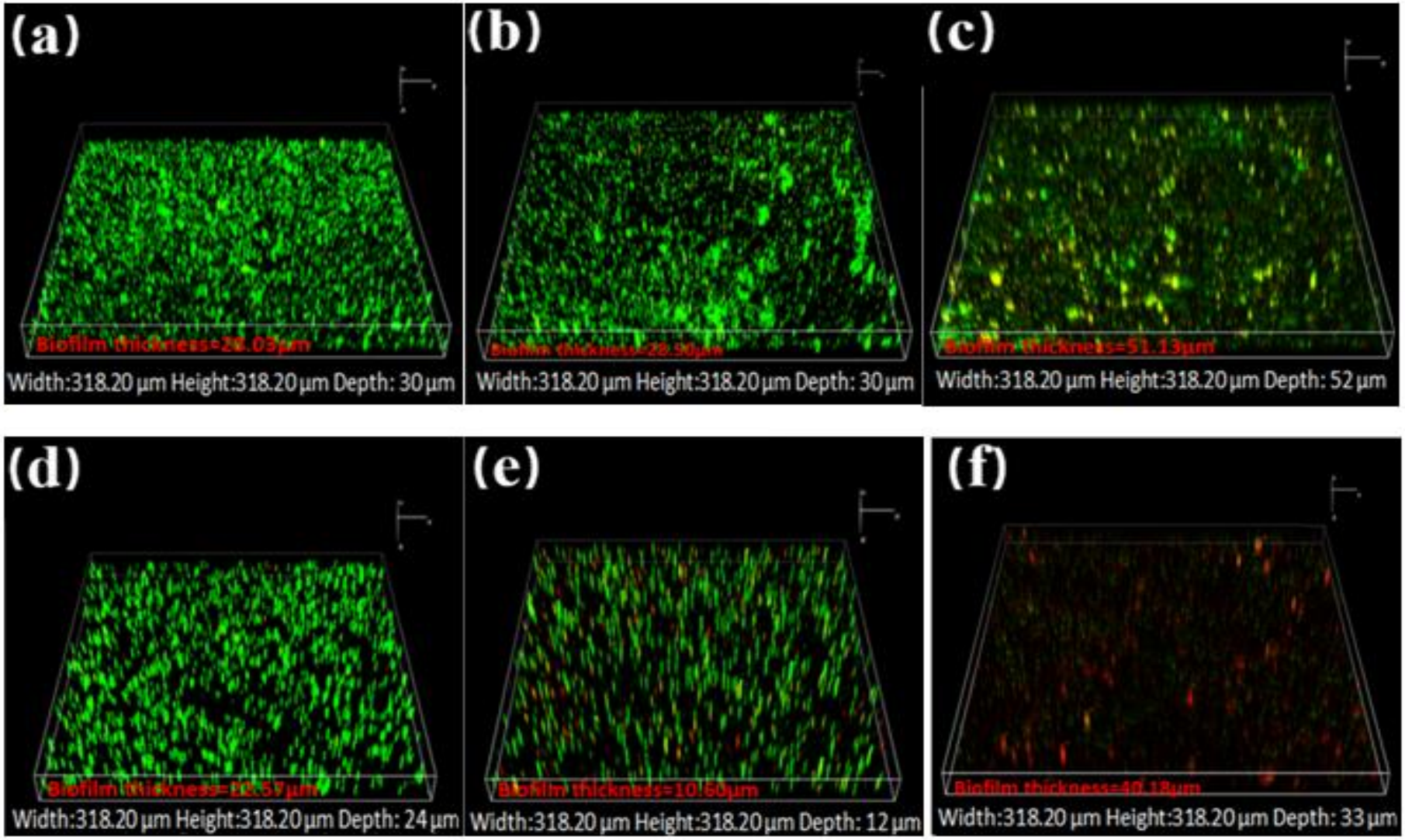
All >10%Cu

3D reconstruction of the atom positions and isoconcentration surface for regions containing >10% Cu for Fe, Cr, Cu, Mo, Ni, C and N based on the orange isosurfaces.

Copper was "evenly" distributed in the 2205-Cu DSS.

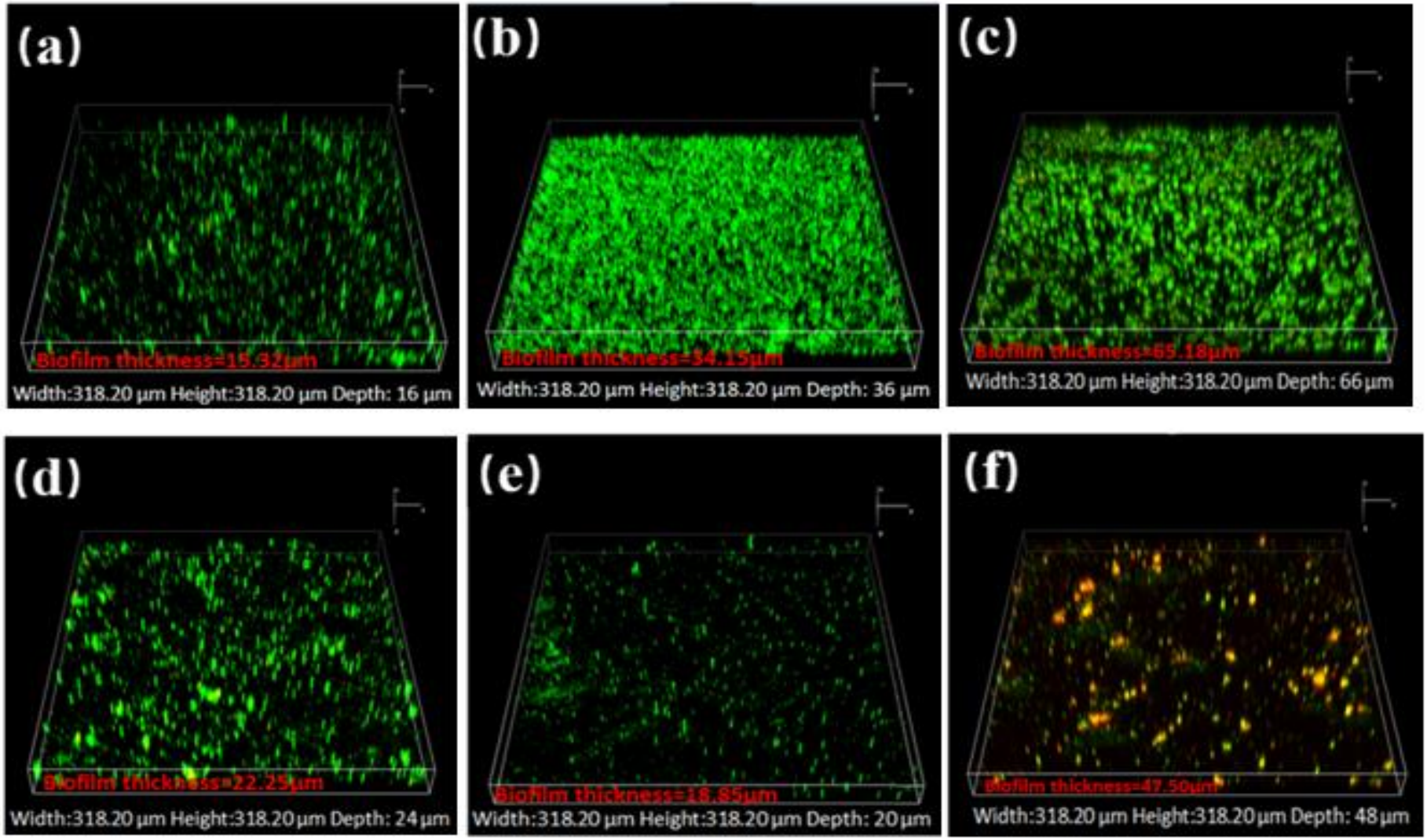
2205-Cu DSS mitigated corrosive biofilm

Initial inoculation of 10^5 cells/ml *P. aeruginosa* in artificial seawater for 1, 3, 5 days.



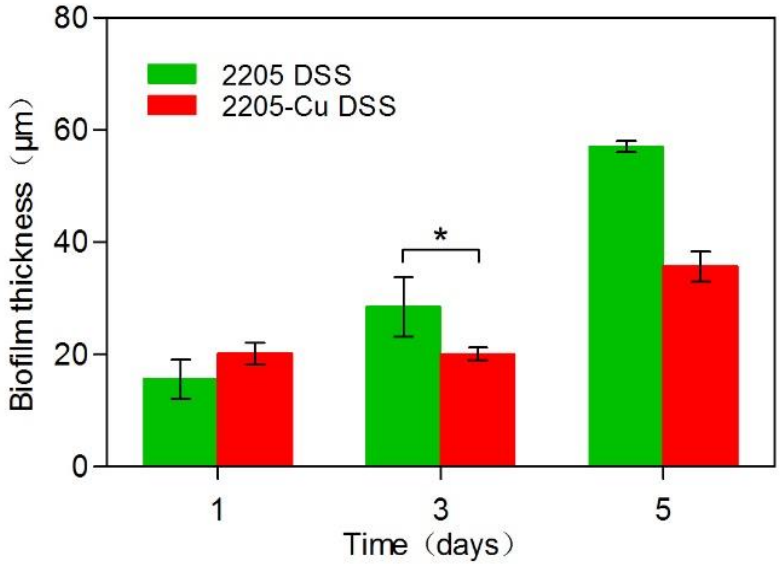
2205-Cu DSS mitigated corrosive biofilm

Initial inoculation of 10^3 cells/ml *P. aeruginosa* in artificial seawater for 1, 3, 5 days.



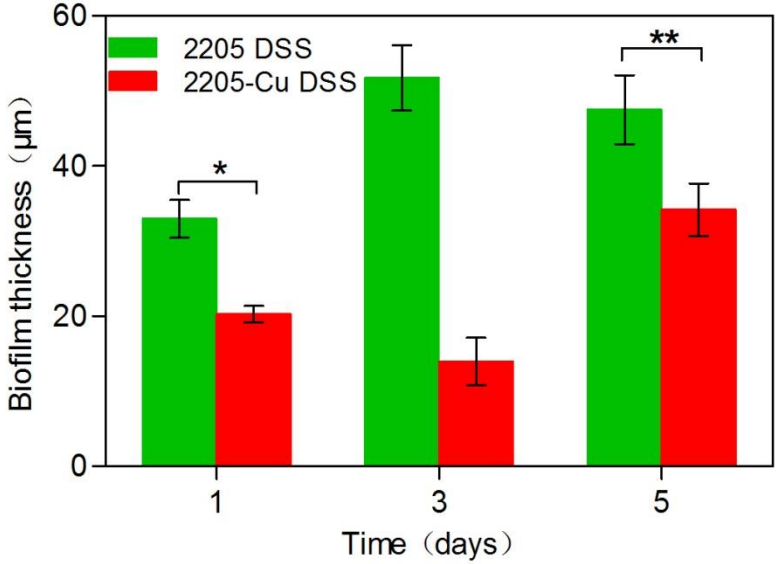
2205-Cu DSS mitigated corrosive biofilm

(a)

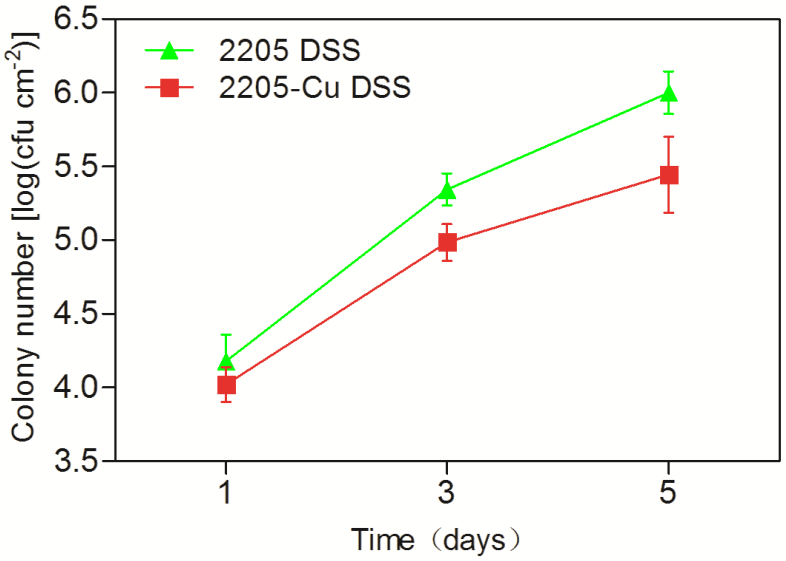


10^3 cells/ml inoculation

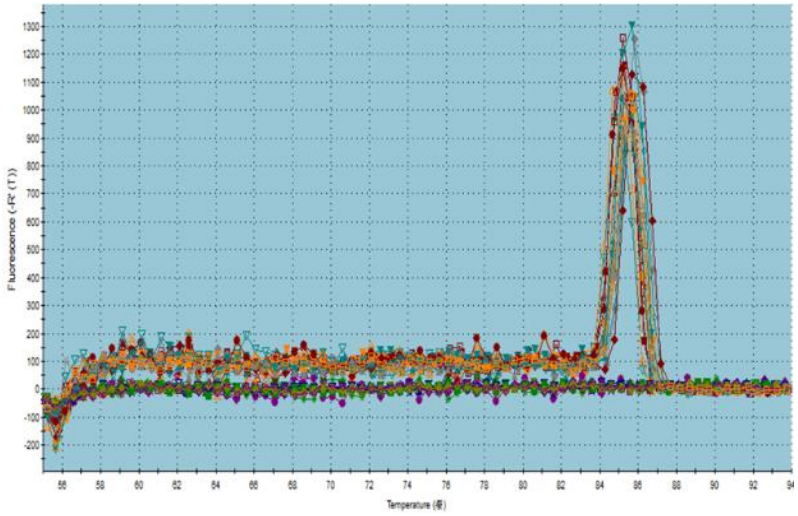
(b)

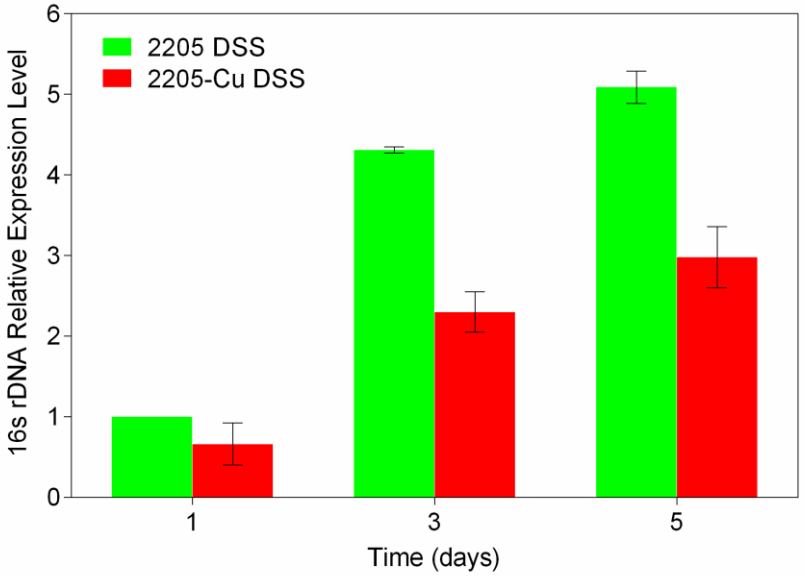


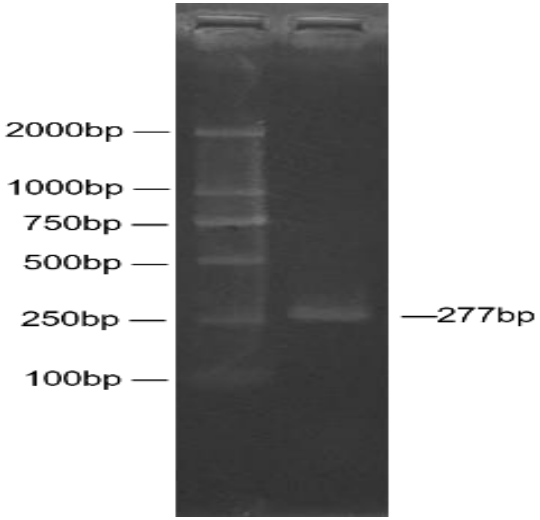
10^5 cells/ml inoculation



2205-Cu DSS mitigated corrosive biofilm





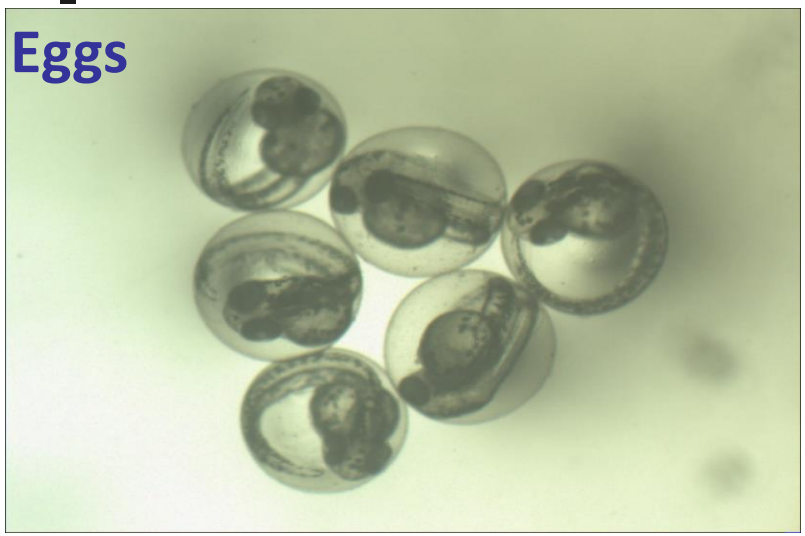


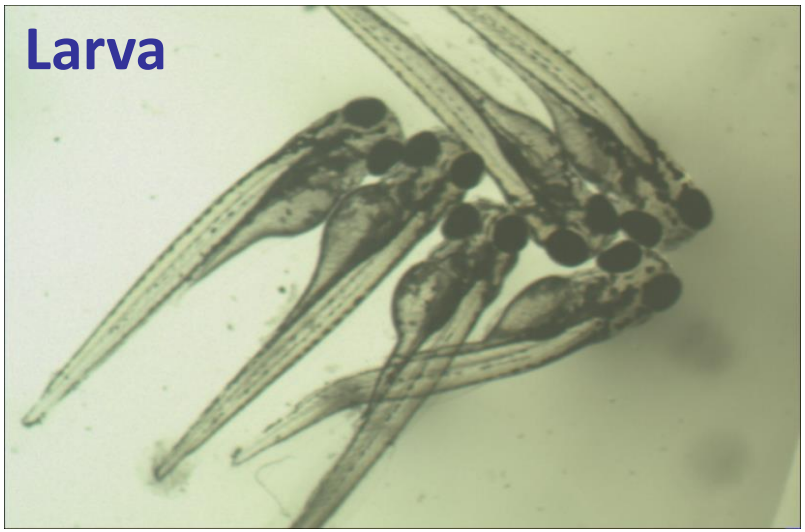
Forward primer：
5’-AGACACCGTCCAGACTCCTAC-3’

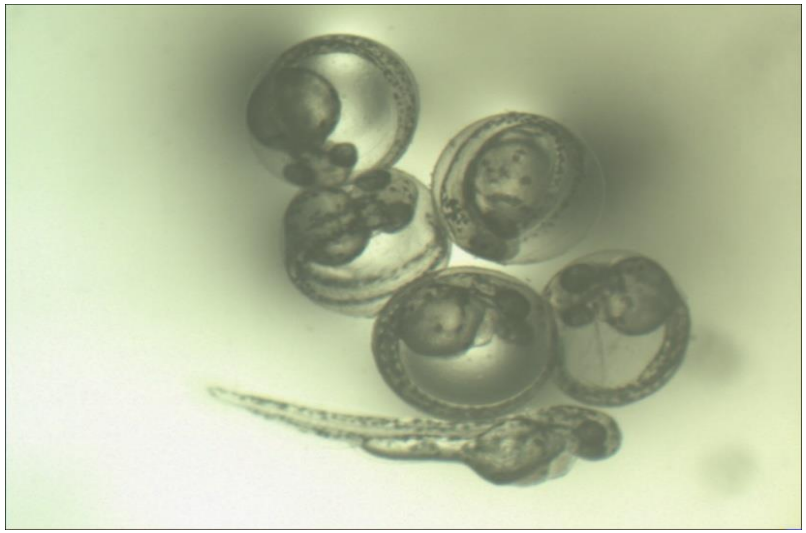
Reverse primer：
5’-CCAACTTGCTGAACCACCTAC-3’

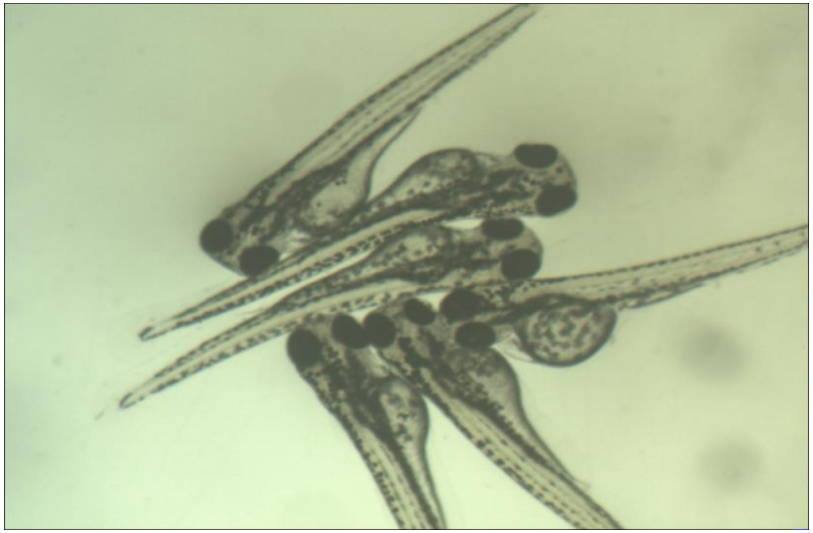
Quantitative PCR further confirmed the strong antibacterial ability of 2205 Cu-DSS.

Environmental toxicity of 2205-Cu DSS





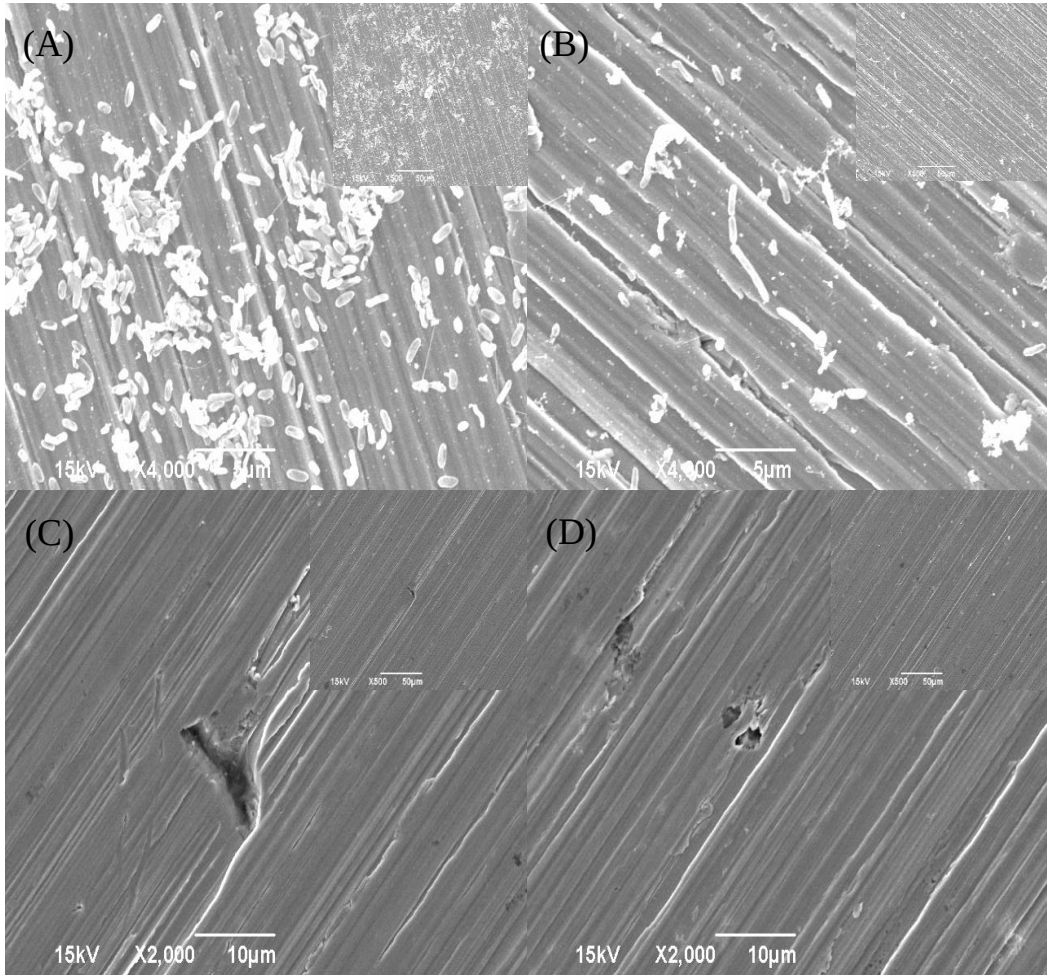


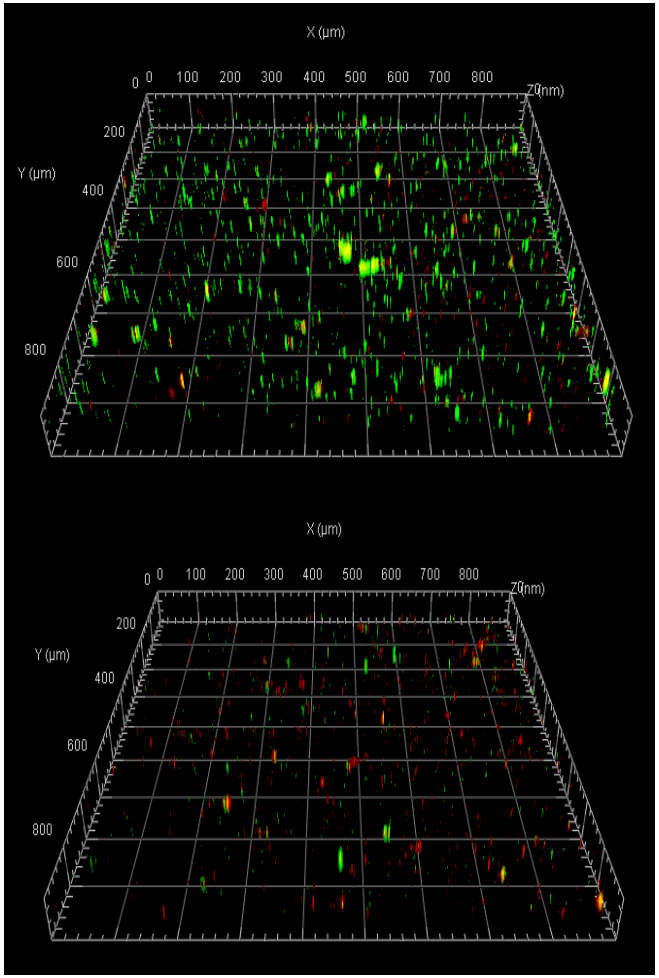


No death and abnormality

2205 Cu-DSS was environmentally safe.

2205-Cu DSS mitigated corrosive biofilm

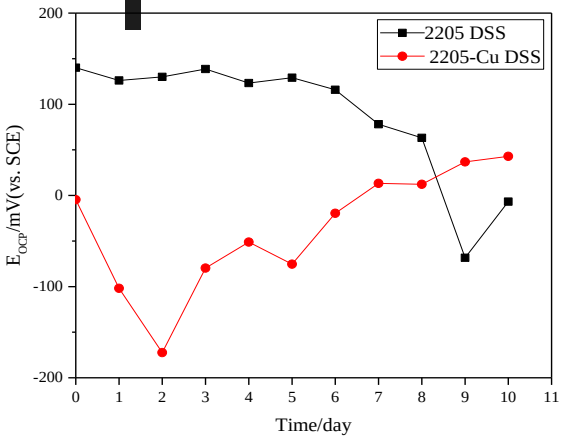


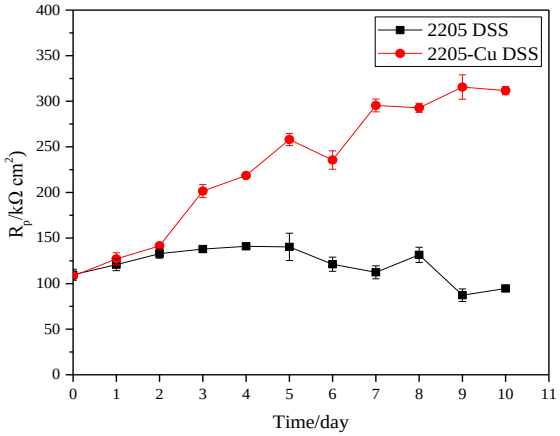


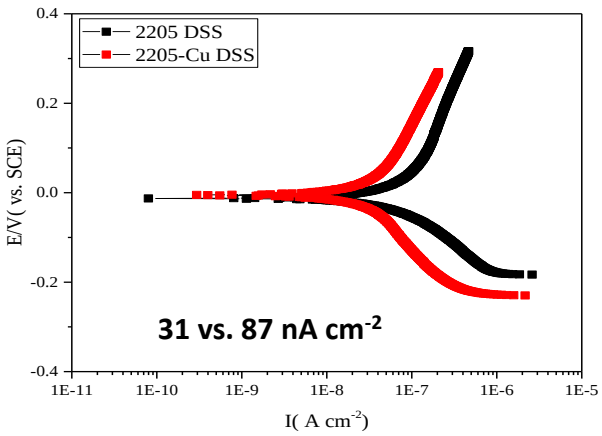
Biofilm and pit morphology of 2205 DSS (A, C) and 2205-Cu DSS (B, D) after the 7-day incubation with nitrate reducing *Pseudomonas aeruginosa* PAO1 in anaerobic condition. Data provided by Prof Tingyue Gu, Ohio University.

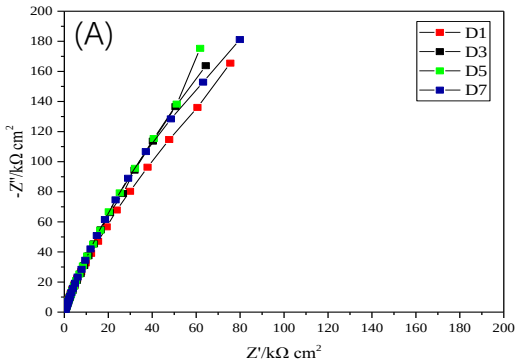
2205 Cu-DSS effectively mitigated anaerobic biofilm.

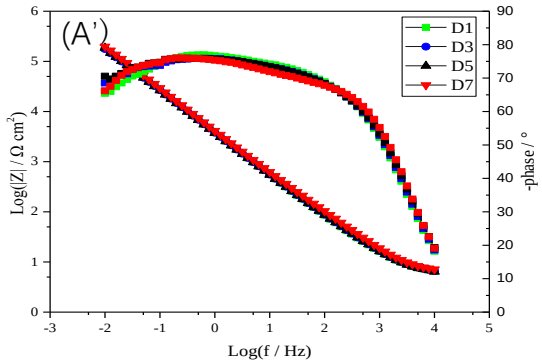
2205-Cu DSS mitigated MIC

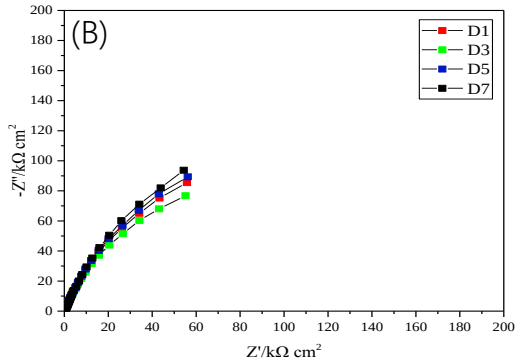


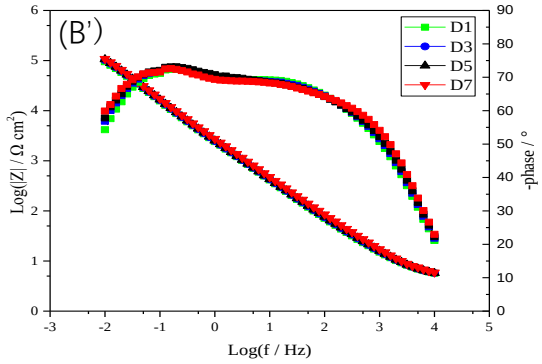


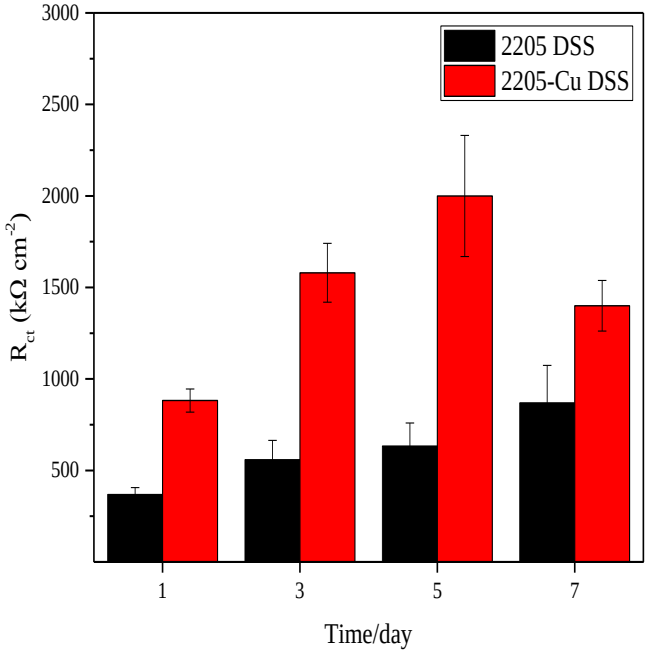








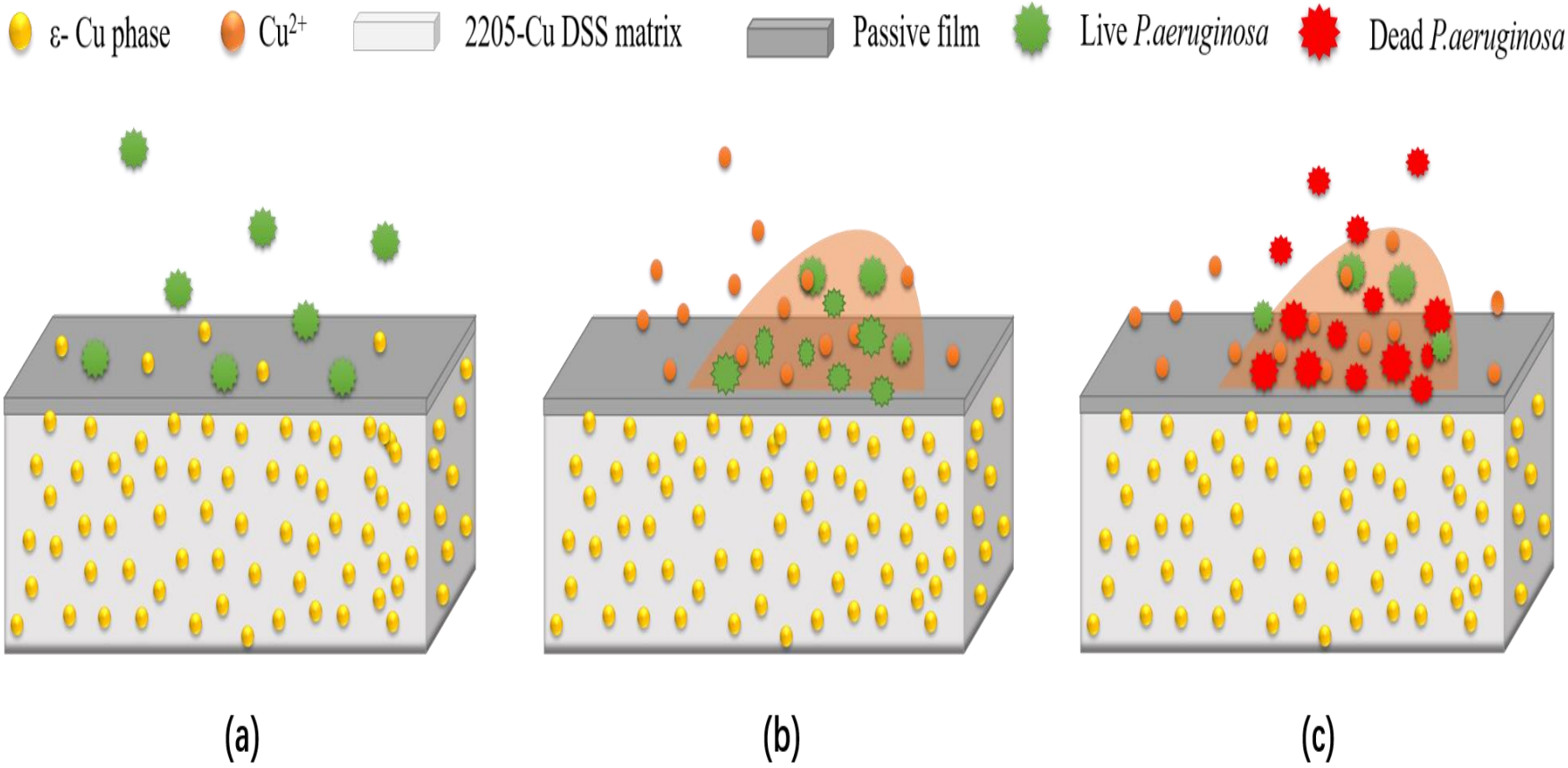




2205 Cu-DSS effectively mitigated anaerobic MIC.

2205-Cu DSS mitigated MIC

The possible MIC resistance mechanism



The Cu^{2+} ions released from the Cu-rich phases and the direct contact killing by the ε-Cu phases synergistically mitigated the corrosion biofilm and MIC.

Conclusion:

- **The newly designed 2205-Cu DSS was found to be a potential anti-MIC material used in marine environments.**

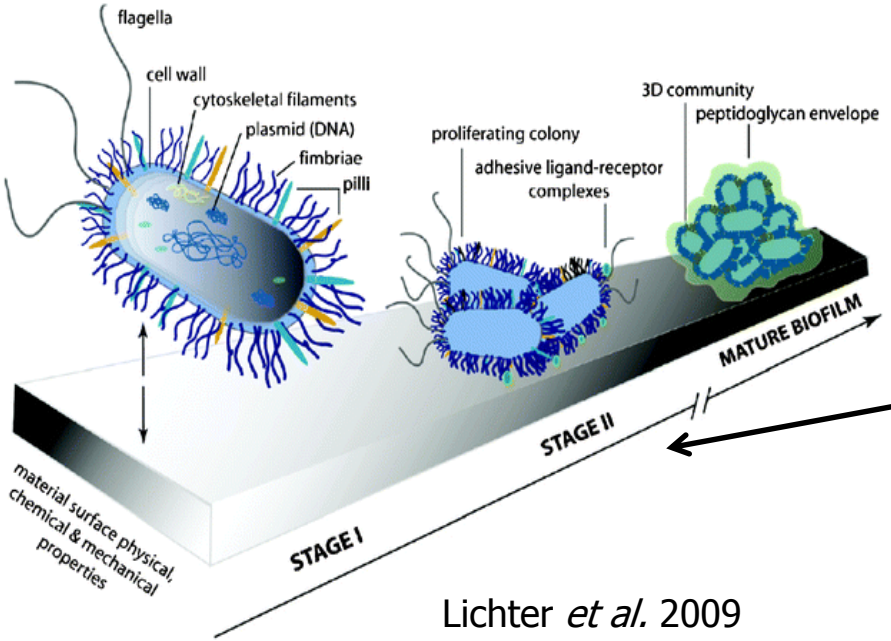
- **The novelty is that a new method is developed to mitigate MIC from the material aspect.**

- **The investigation of 2^{nd} generation 2205-Cu DSS is ongoing to pursue a better antibacterial ability with broad spectrum.**

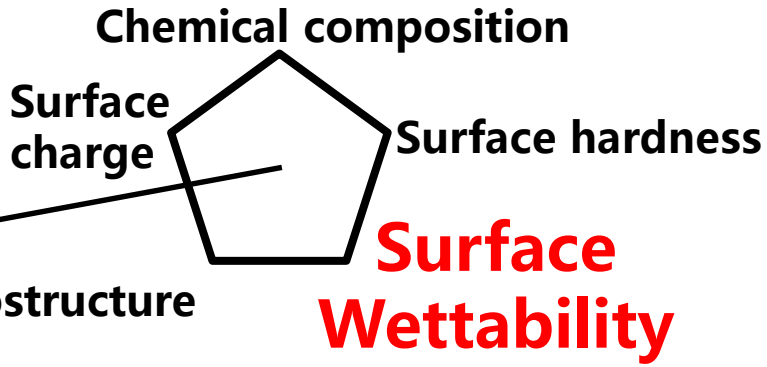
Mussel-inspired superhydrophobic surfaces with enhanced corrosion resistance and dual-action antibacterial and anti-MIC properties

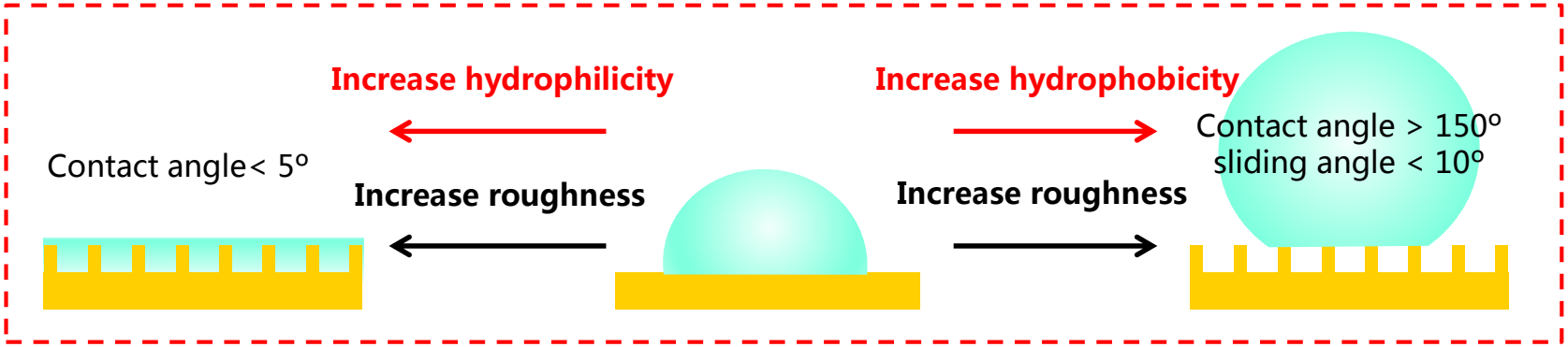
Cooperated with Prof. Dawei Zhang

Background



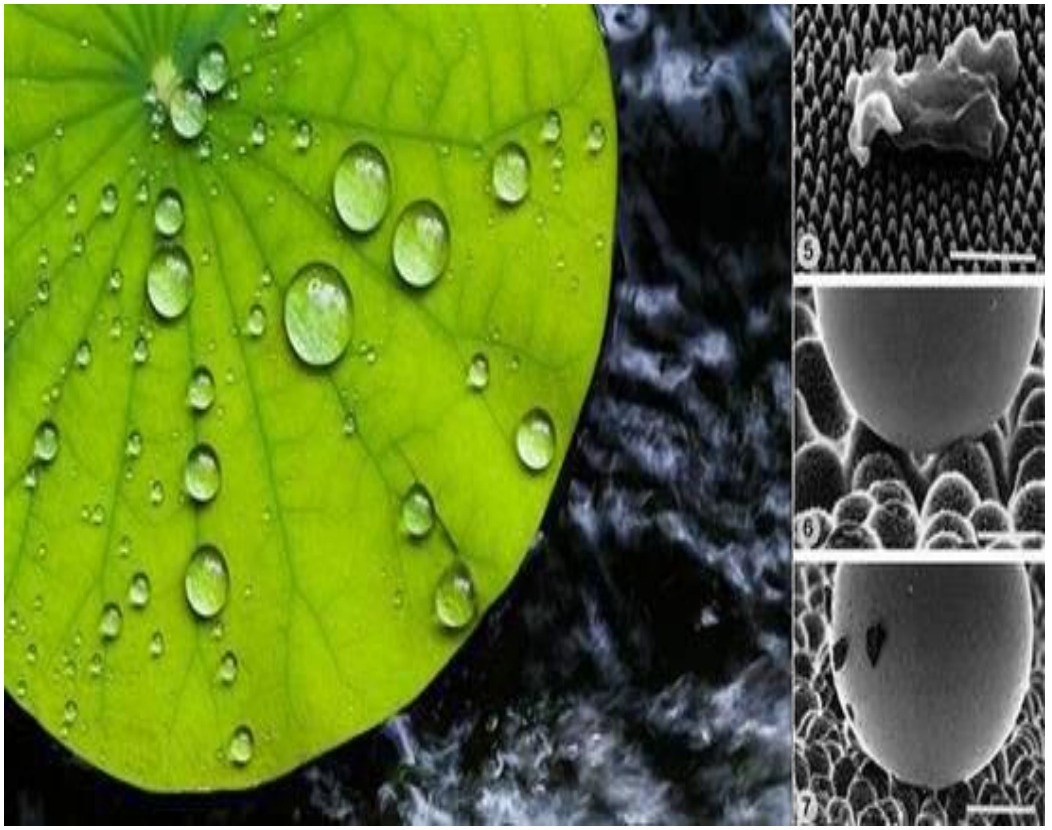
Lichter *et al.* 2009





Improving the hydrophobic (hydrophilic) of the material surface: (1) reducing (improving) the surface energy of the material, (2) changing the surface microstructure and increasing the surface roughness.

Background

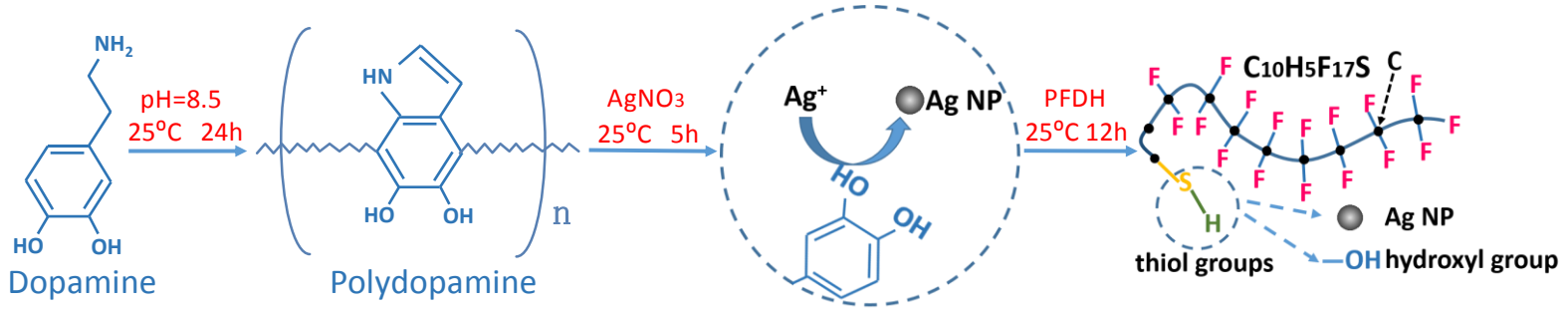


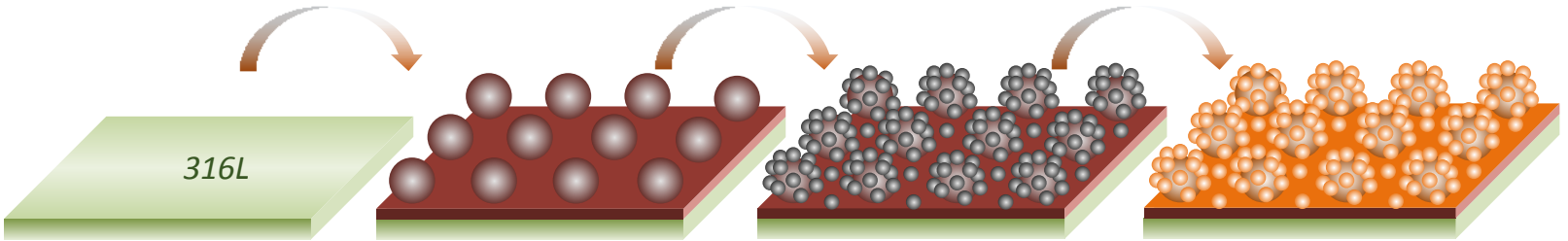
Mimicing the natural nanostructure (superhydrophobic) is not enough to prevent the biofilm formation and attachment.

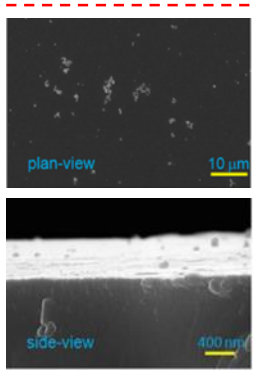
Super-hydrophilic

Super-hydrophobic

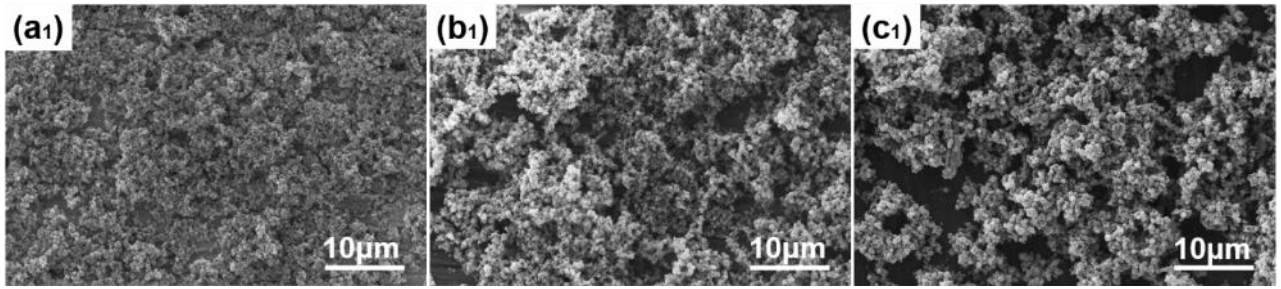
Preparation of superhydrophobic surface







Su *et al.* 2016



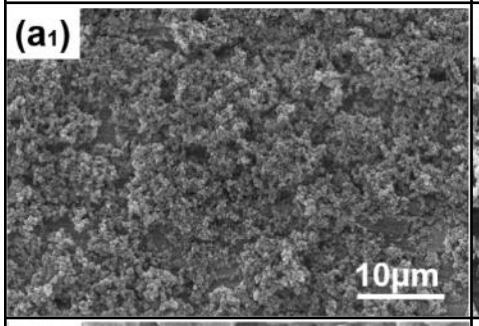
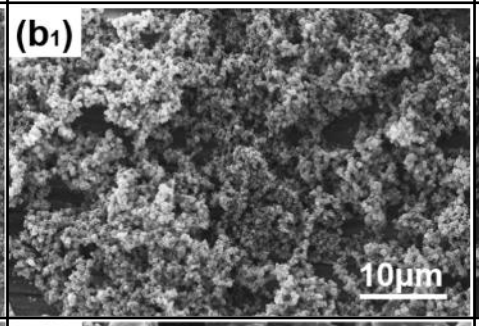
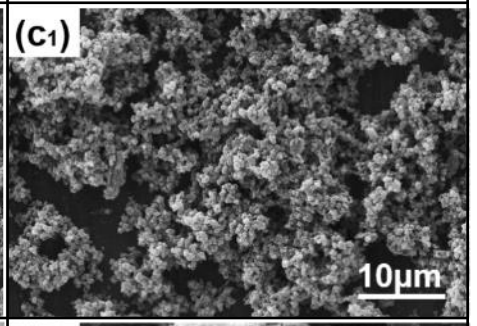
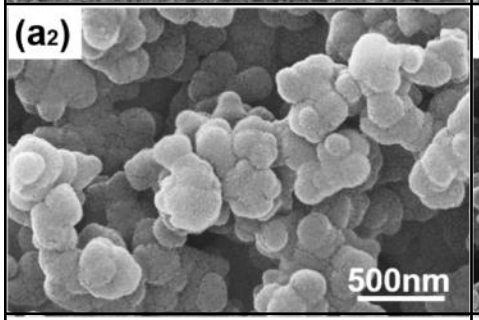
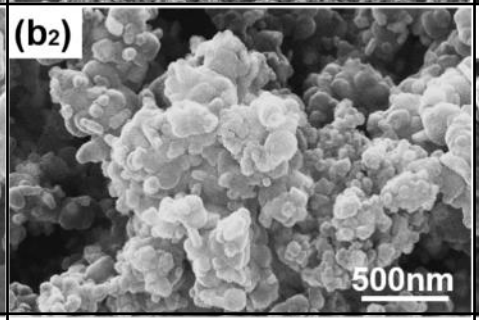
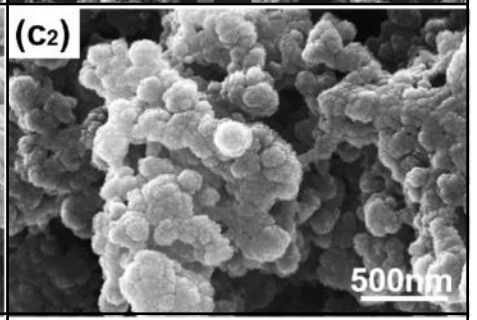
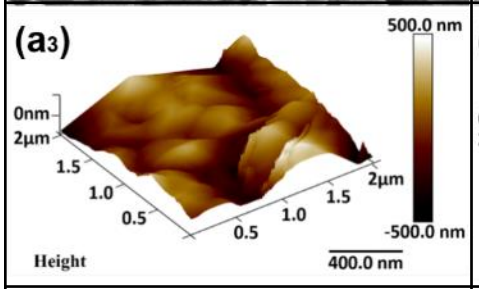
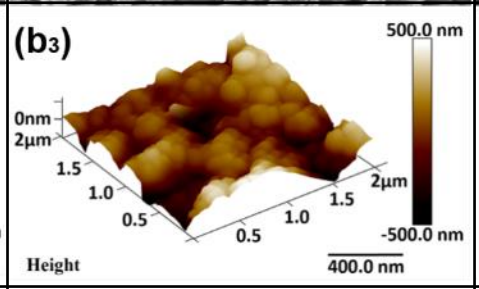
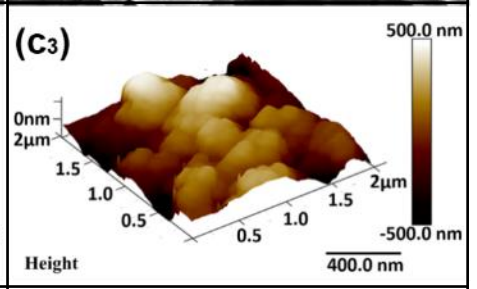
PDA-deposited surface (PDS)

Ag-deposited surface (ADS)

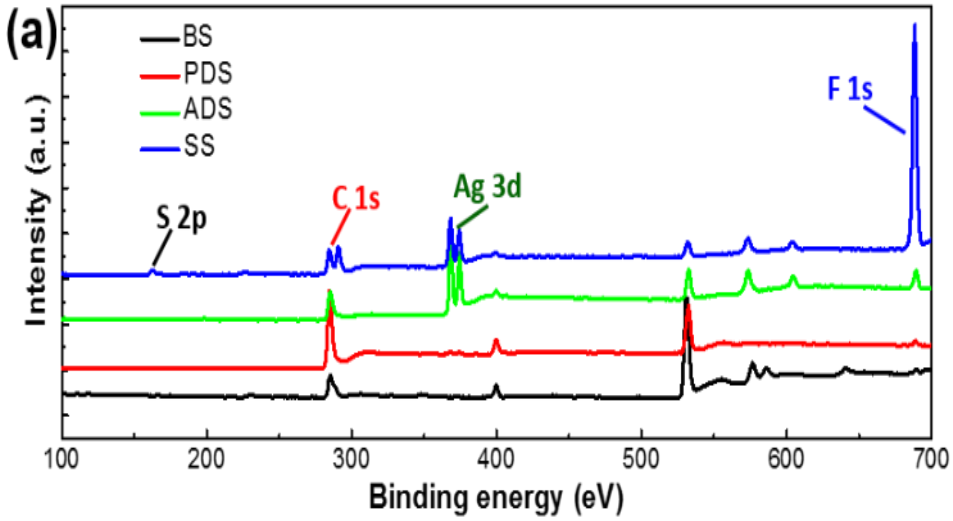
Superhydrophobic surface (SS)

Material Science and Engineering C, 80:566-577, 2017

Surface micro-topography

PDS	ADS	SS
		
		
		
S_a = 124 nm	S_a = 197 nm	S_a = 164 nm

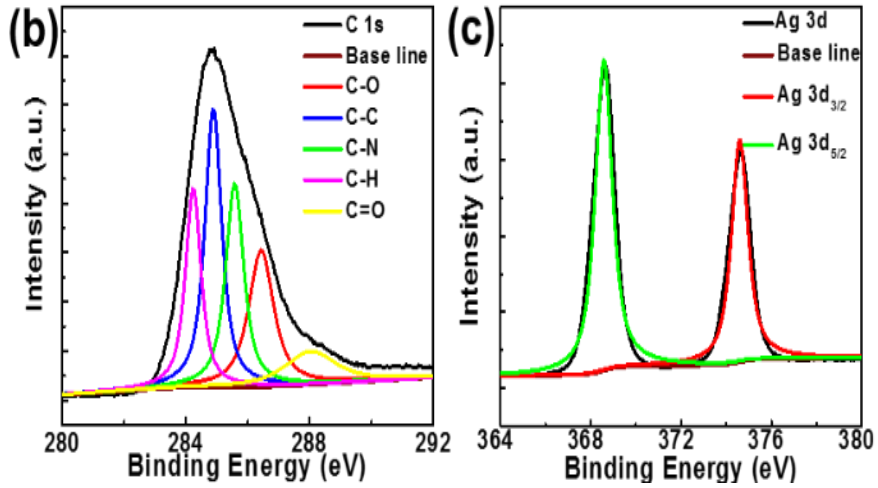
Surface analysis

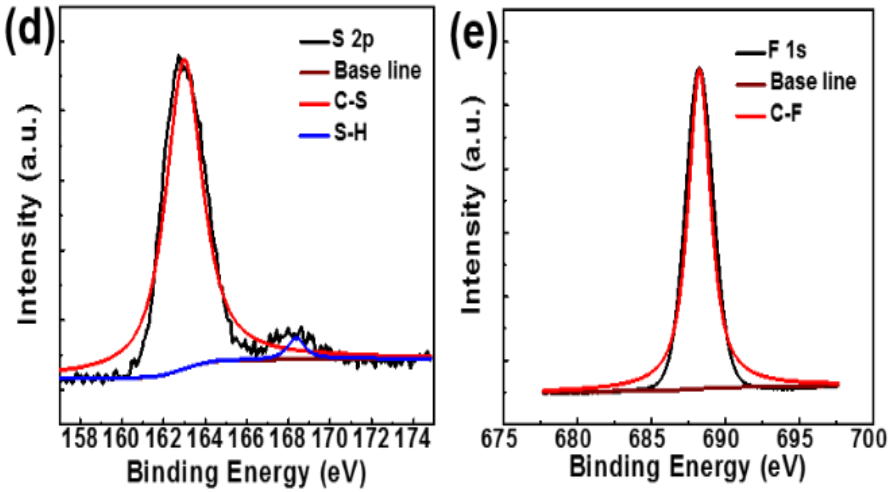


PDS film：C 1s

ADS film：C 1s, Ag 3d

SS film ：C 1s, Ag 3d, S 2p, F 1s



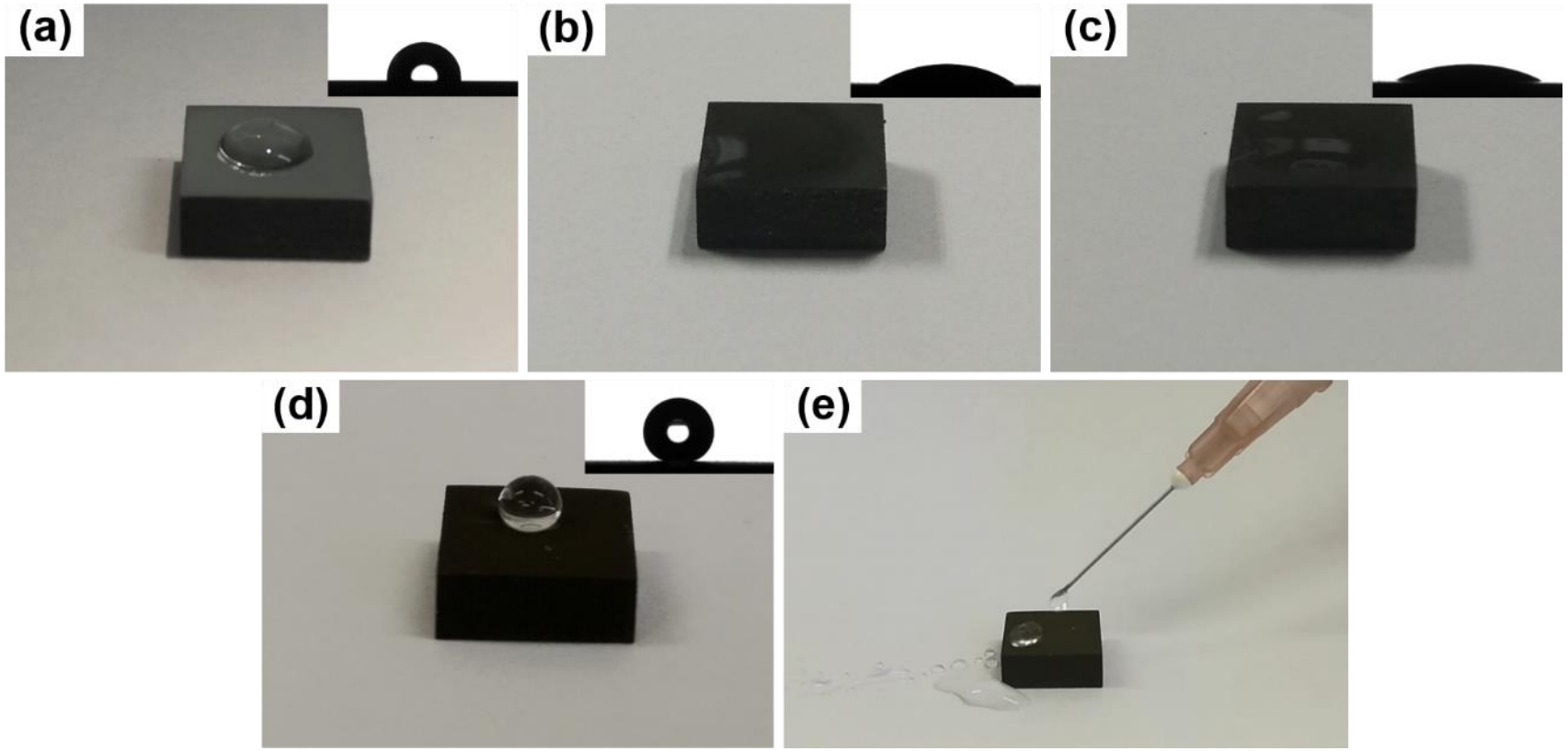


Surface wettability

CA = 80°

CA = 26°

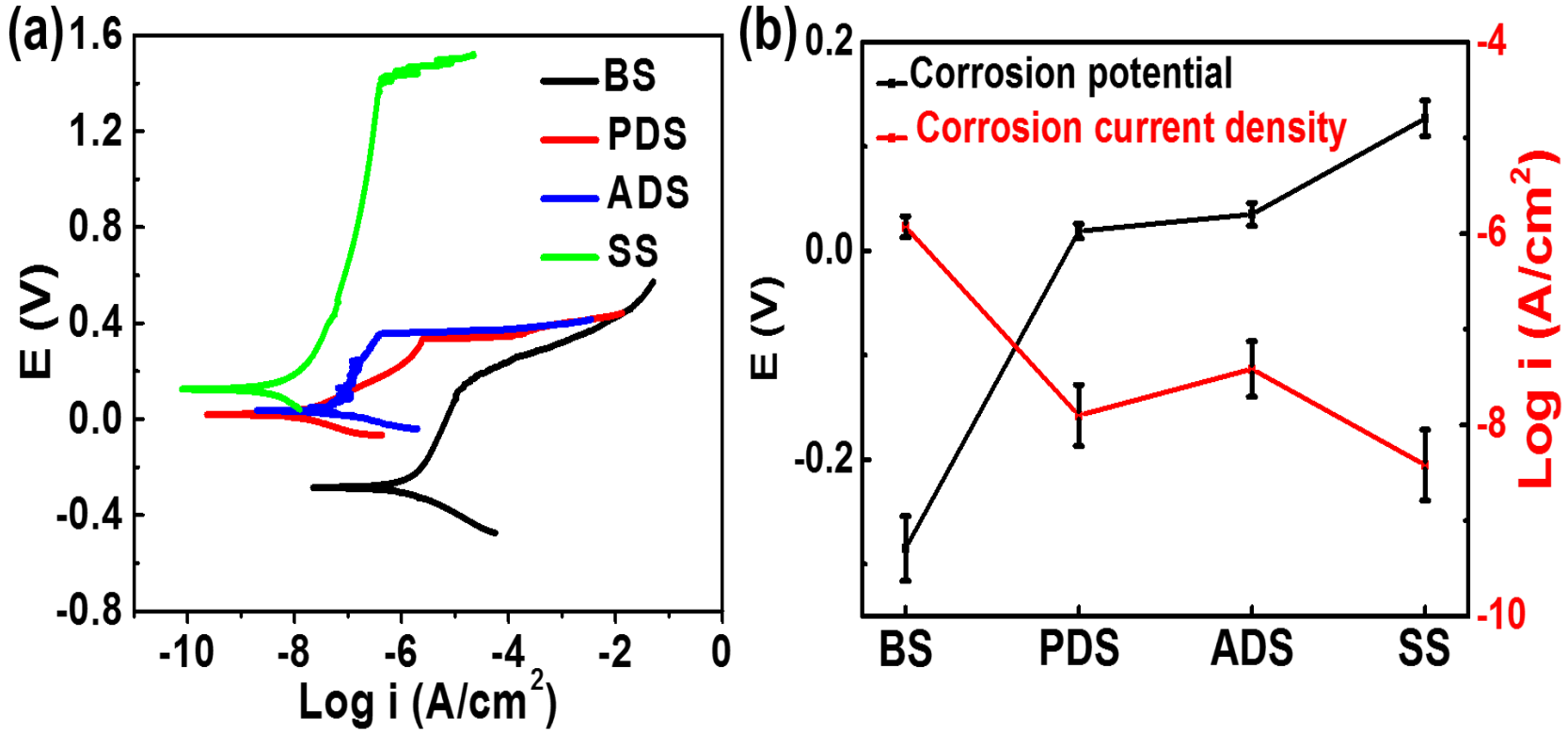
CA = 30°



CA = 153°

SA < 3°

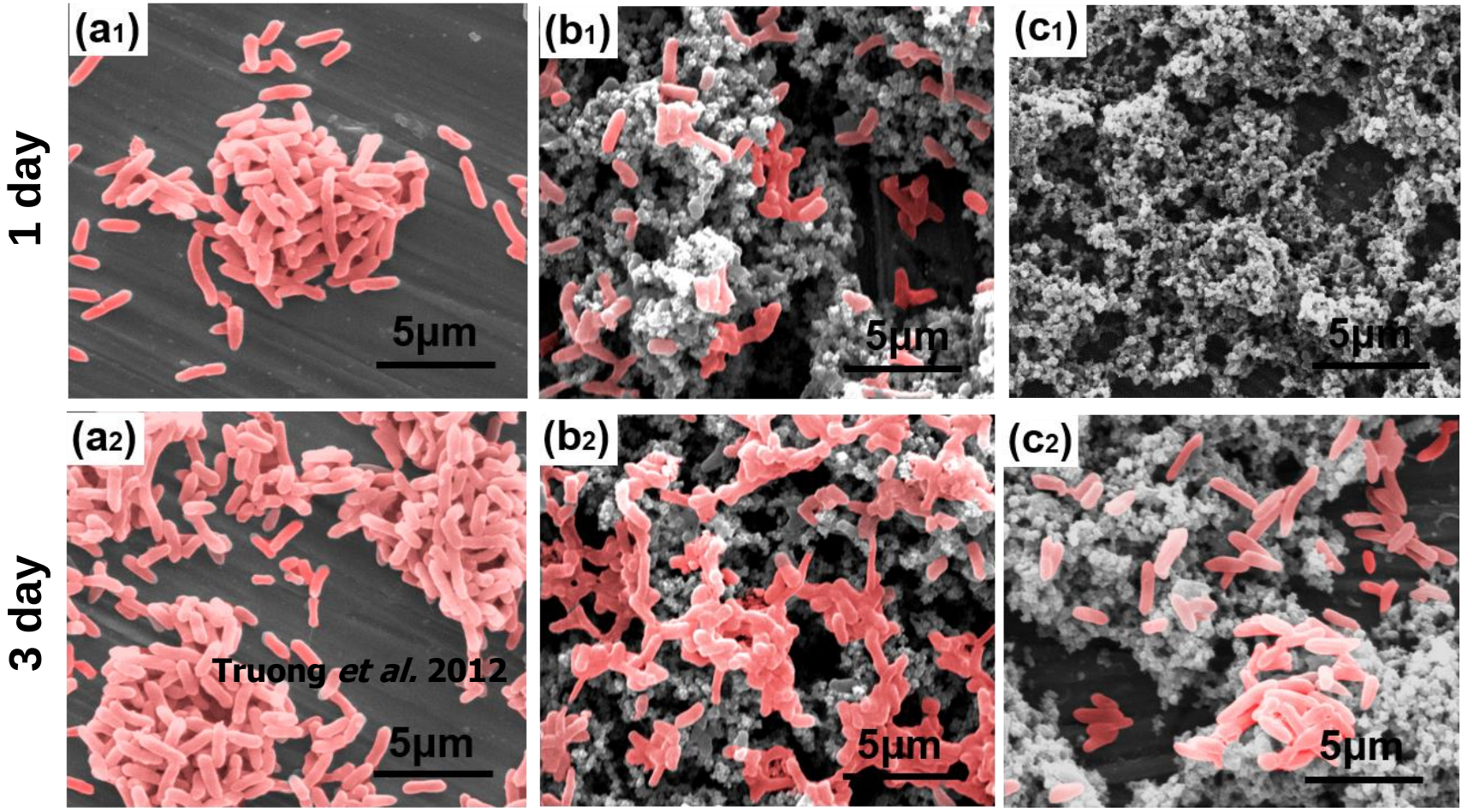
Corrosion resistance



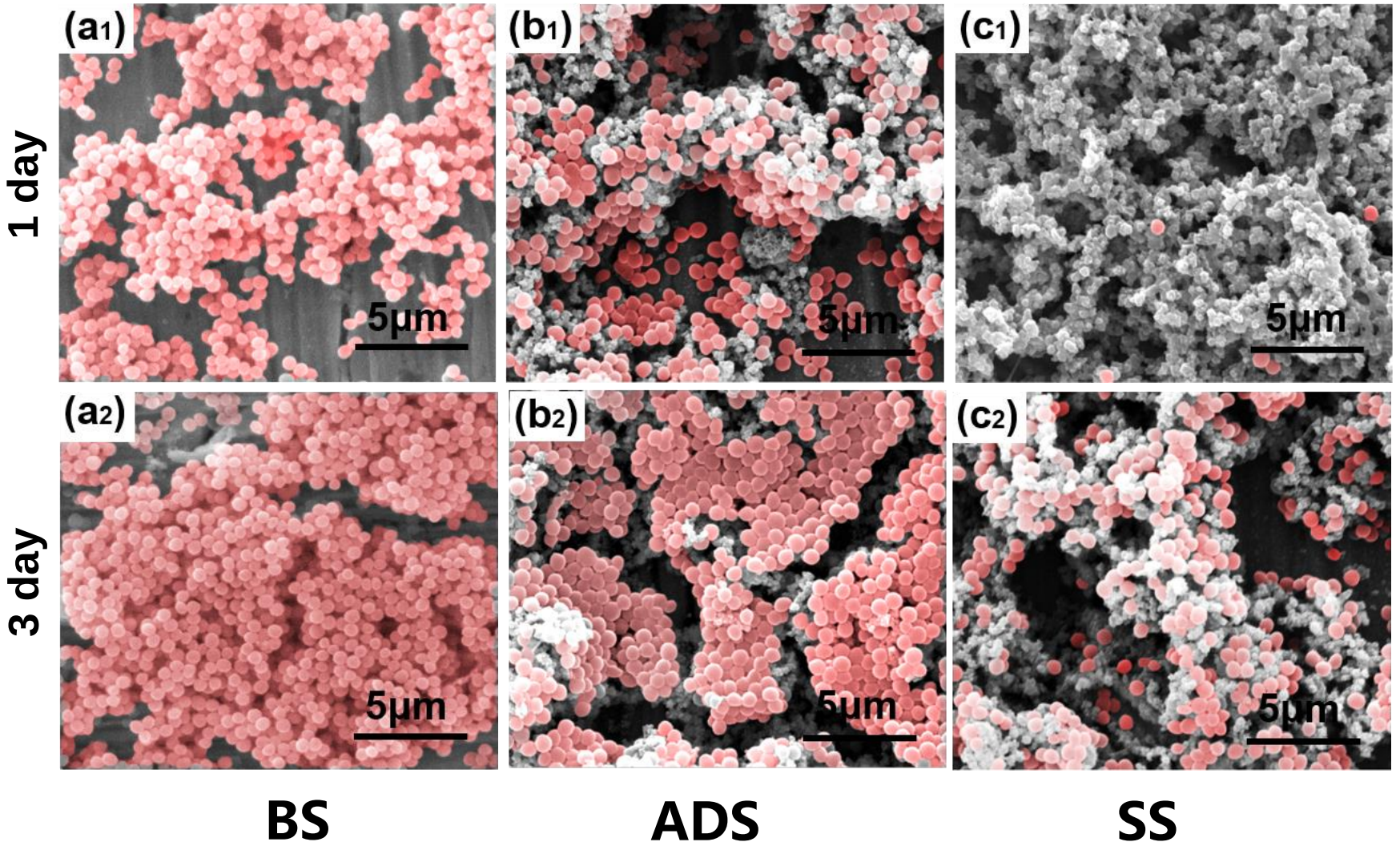
- The chelation of polydopamine (PDA) film with Fe showed a protective effect on stainless steel substrate.

- The gas film formed by the superhydrophobic surface improved the corrosion resistance.

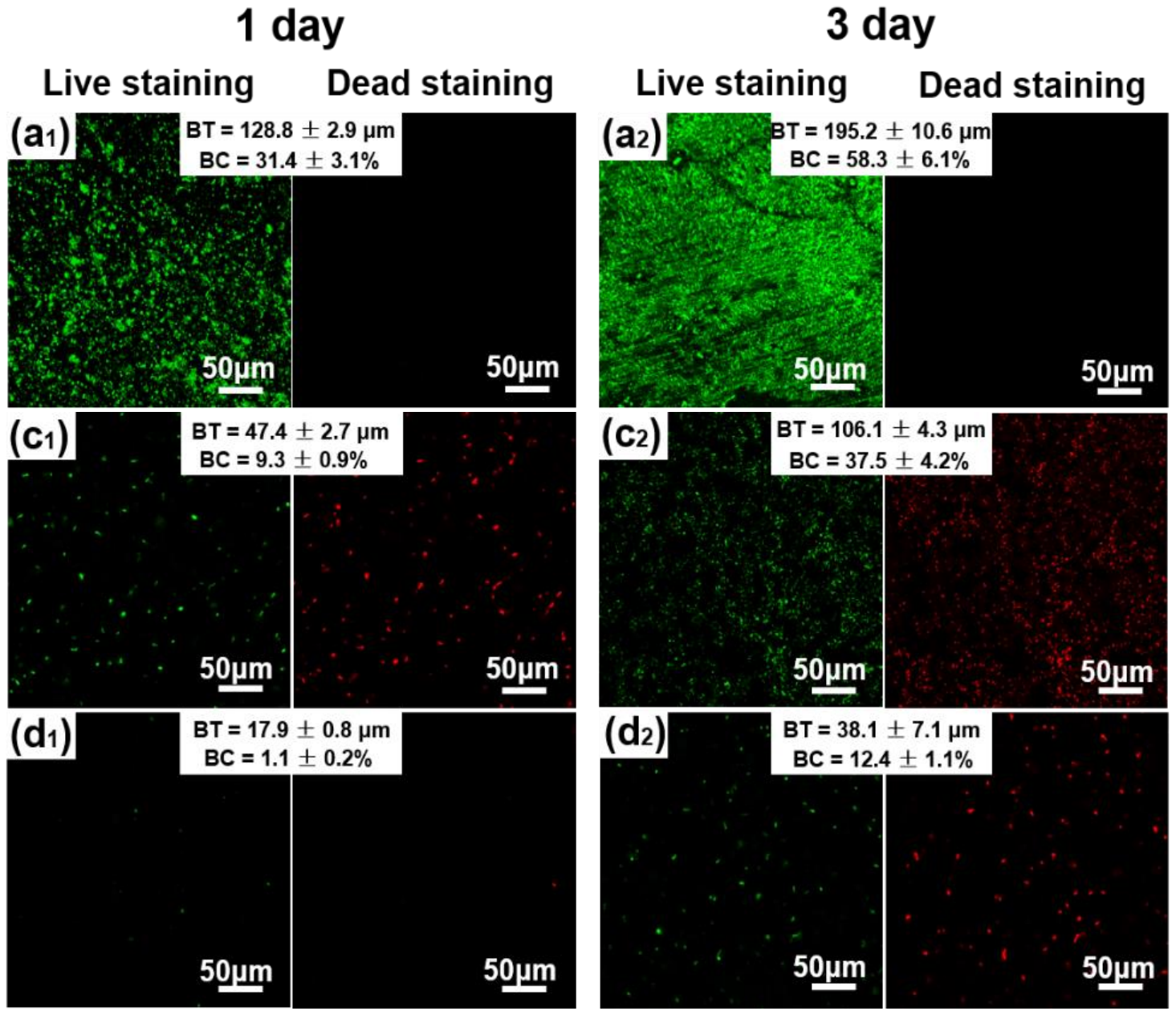
Biofilm prevention of *E. coli*



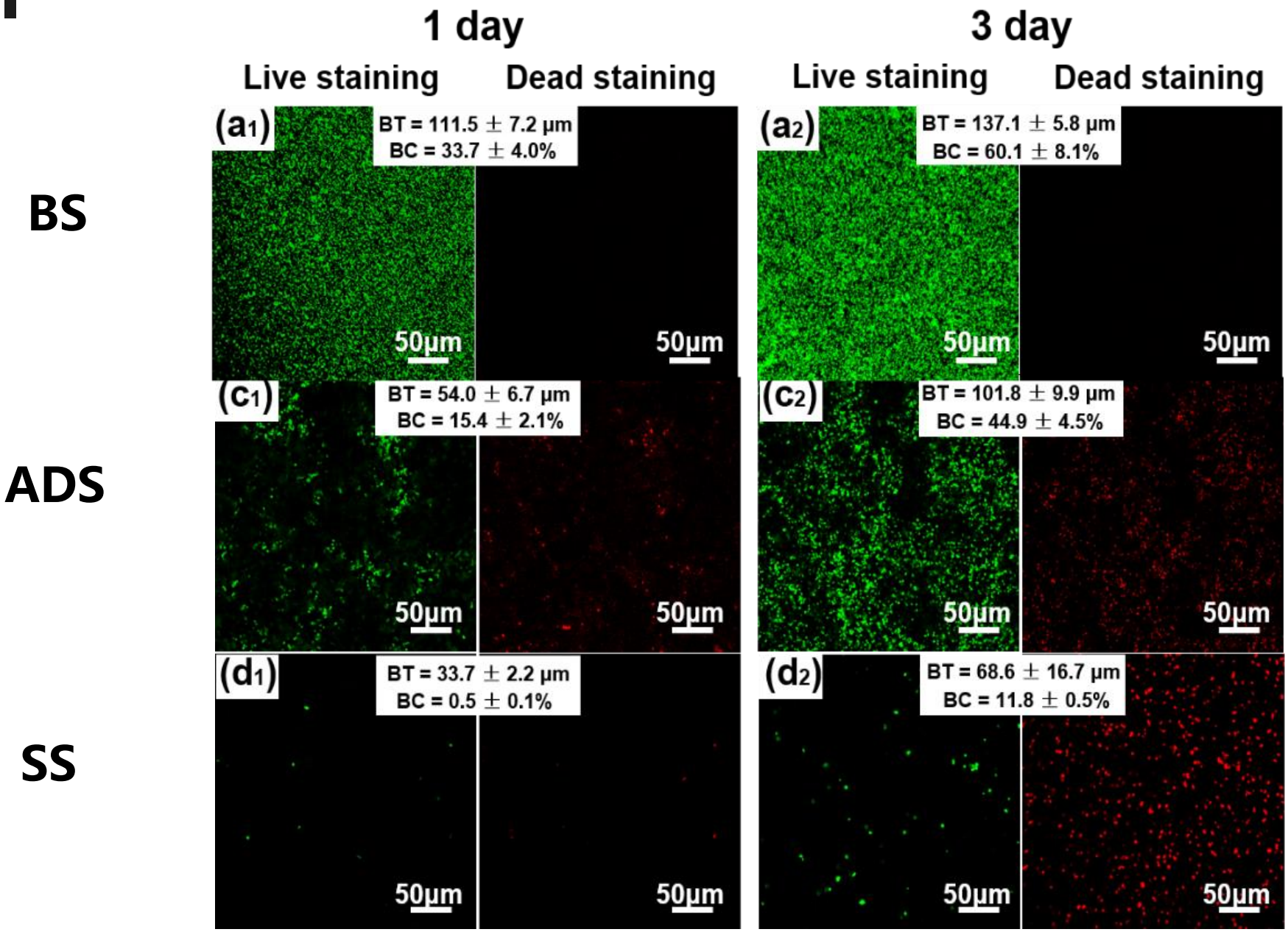
Biofilm prevention of *S. aureus*



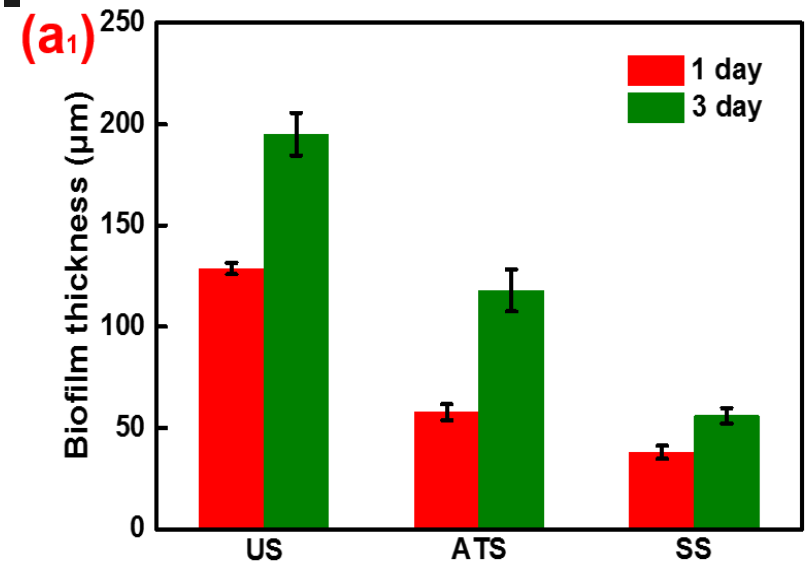
Biofilm mitigation (*E. coli*)

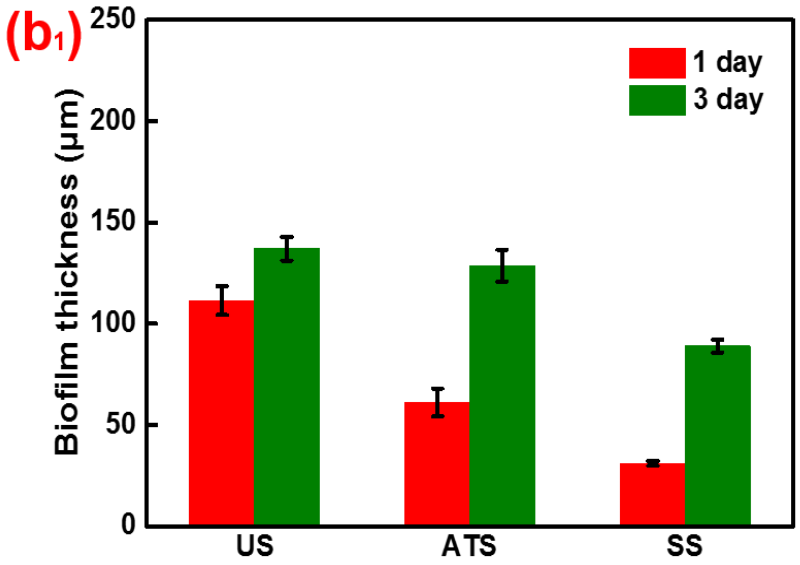


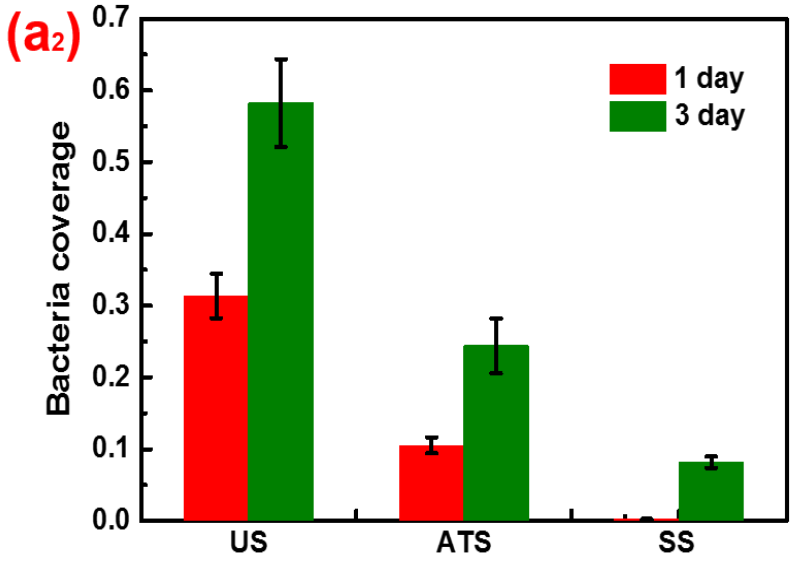
Biofilm mitigation (*S. aureus*)

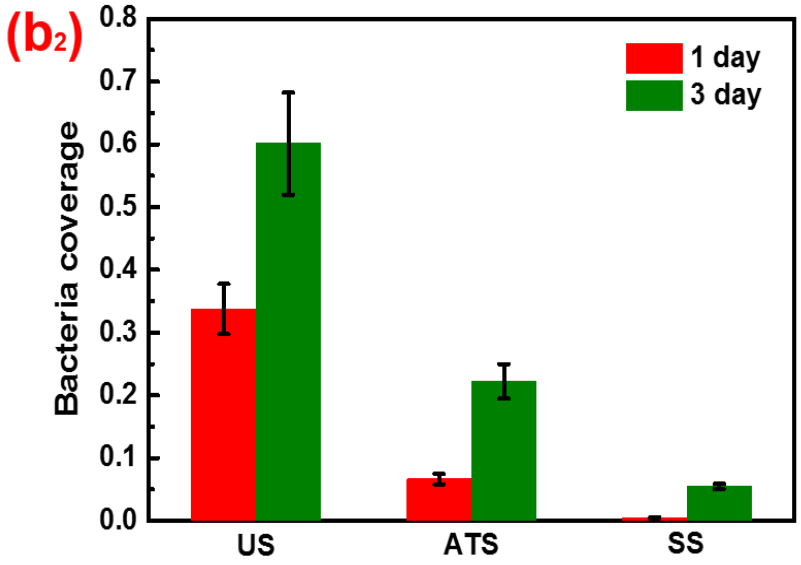


Biofilm thickness and coverage

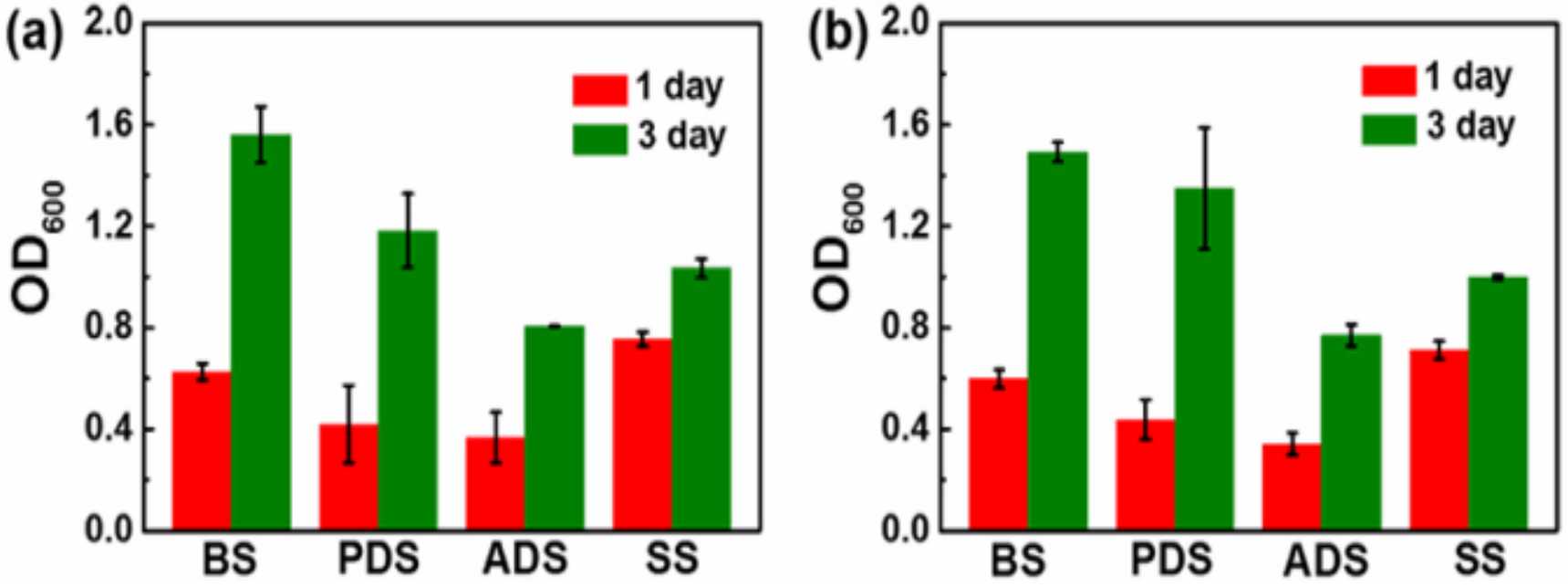








Planktonic cell inhibition (OD_{600nm})



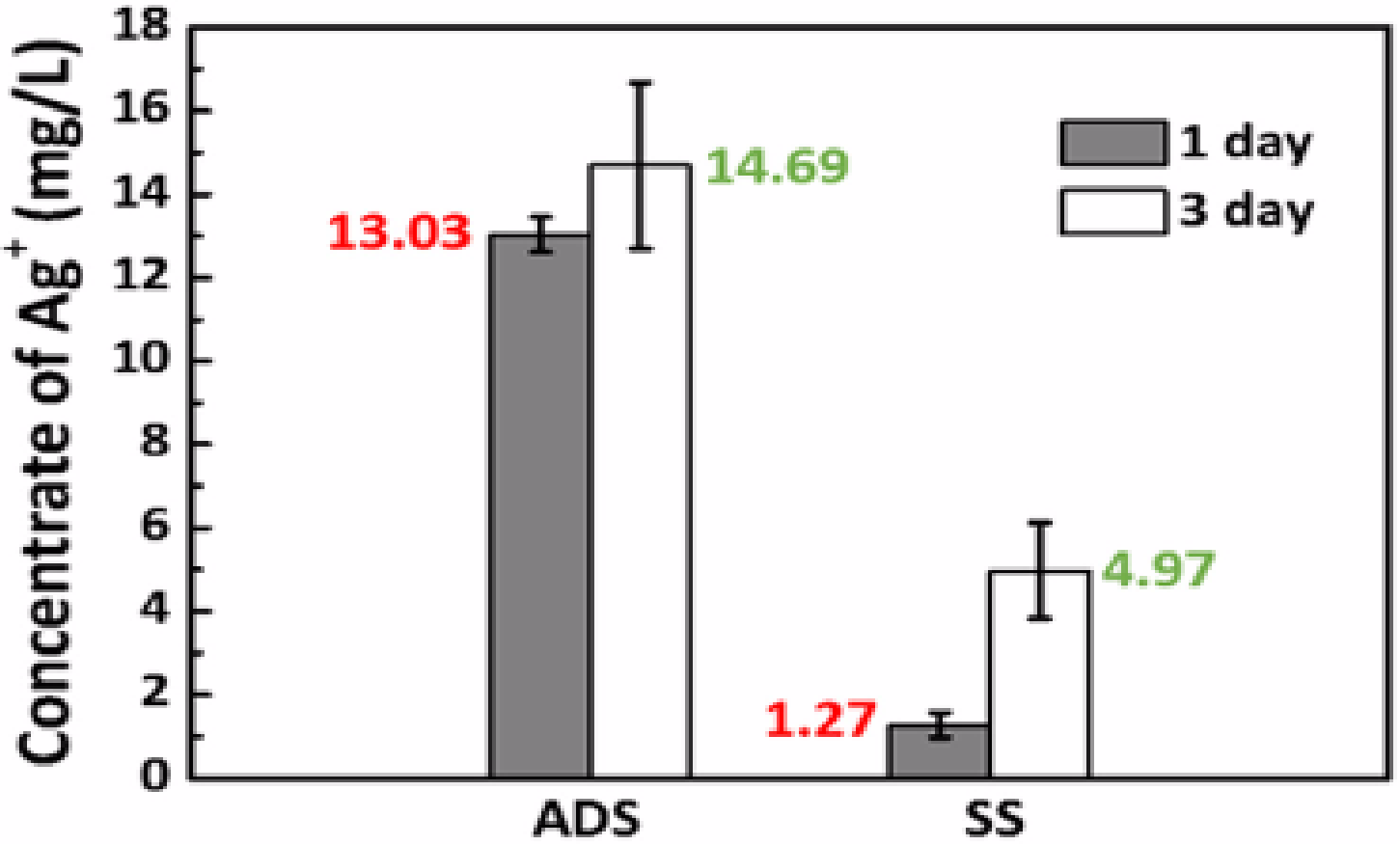
1 day: SS > BS > ADS

3 day: BS > SS > ADS

1 day: the superhydrophobic surface inhibited the attachment of the biofilm, most of the bacteria were in planktonic status, leading to a high OD value of the SS.

3 day: with the release of Ag^+ from SS, the growing of bacteria was inhibited, so the increase rate of the OD value significantly decreased.

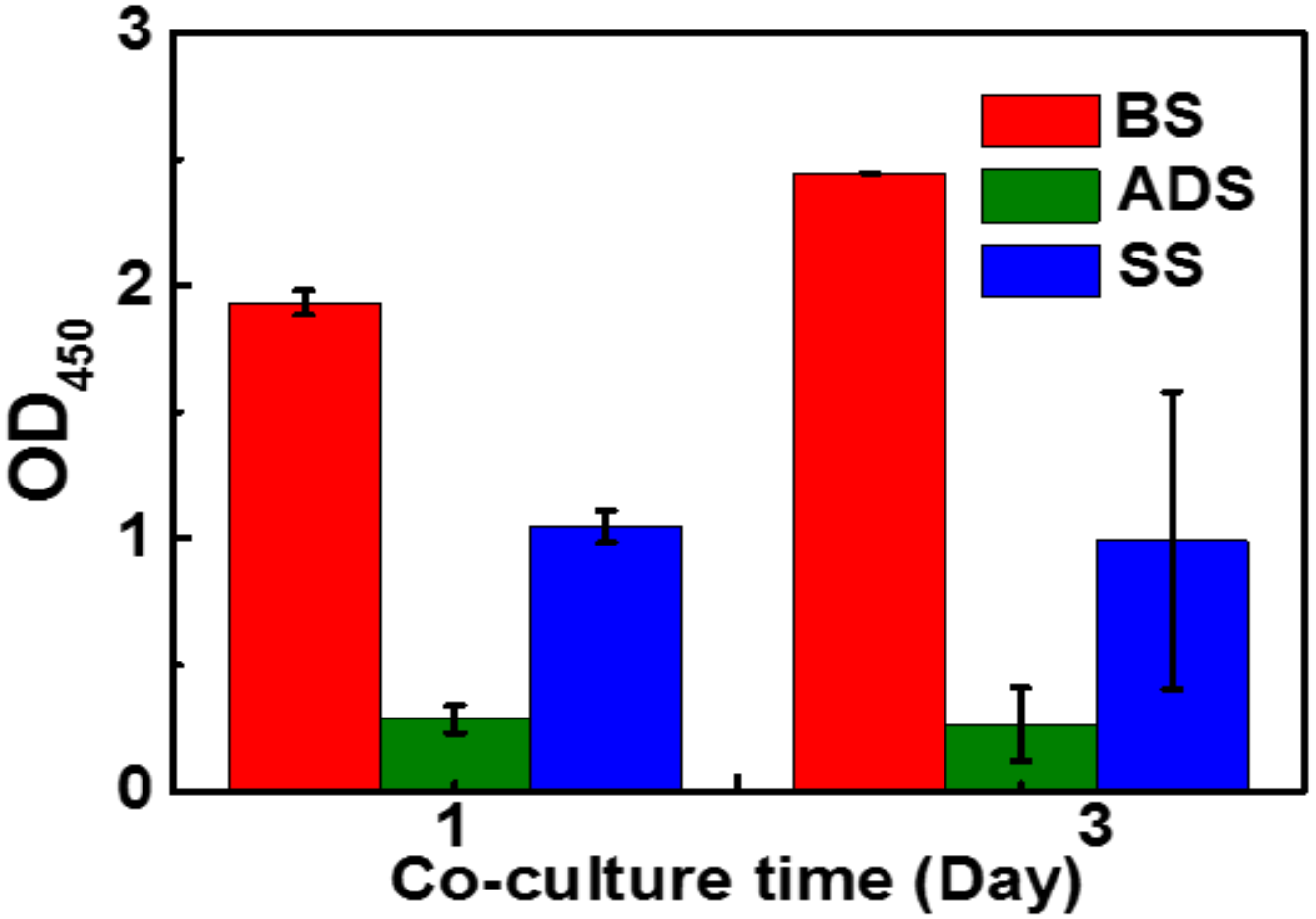
Release of Ag^+



☐ The fast release of Ag^+ from nanosilver surface at the beginning of immersing was not good for long-term antibacterial effect.

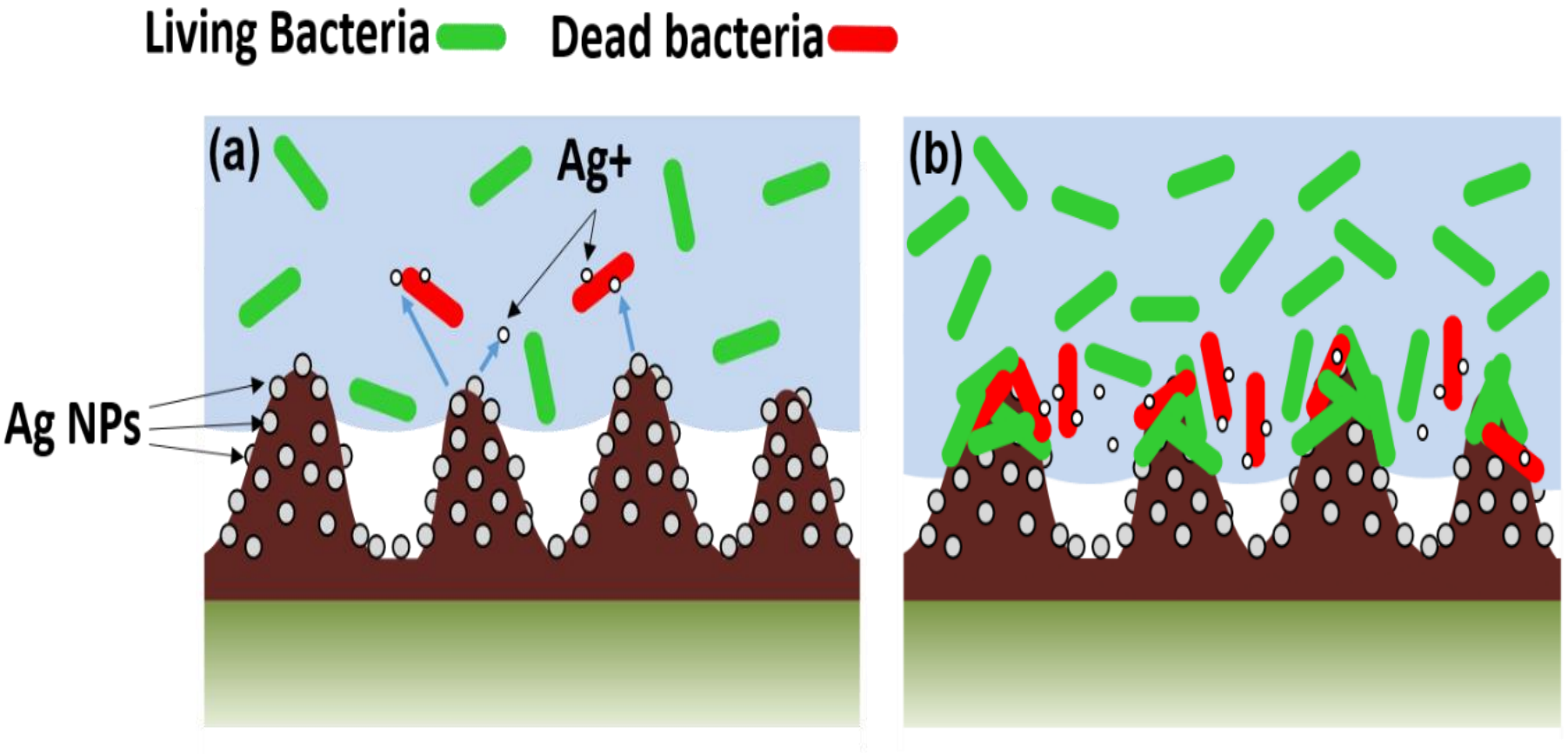
☐ The superhydrophobic surface gradually released Ag^+.

Cytotoxicity (CCK-8)



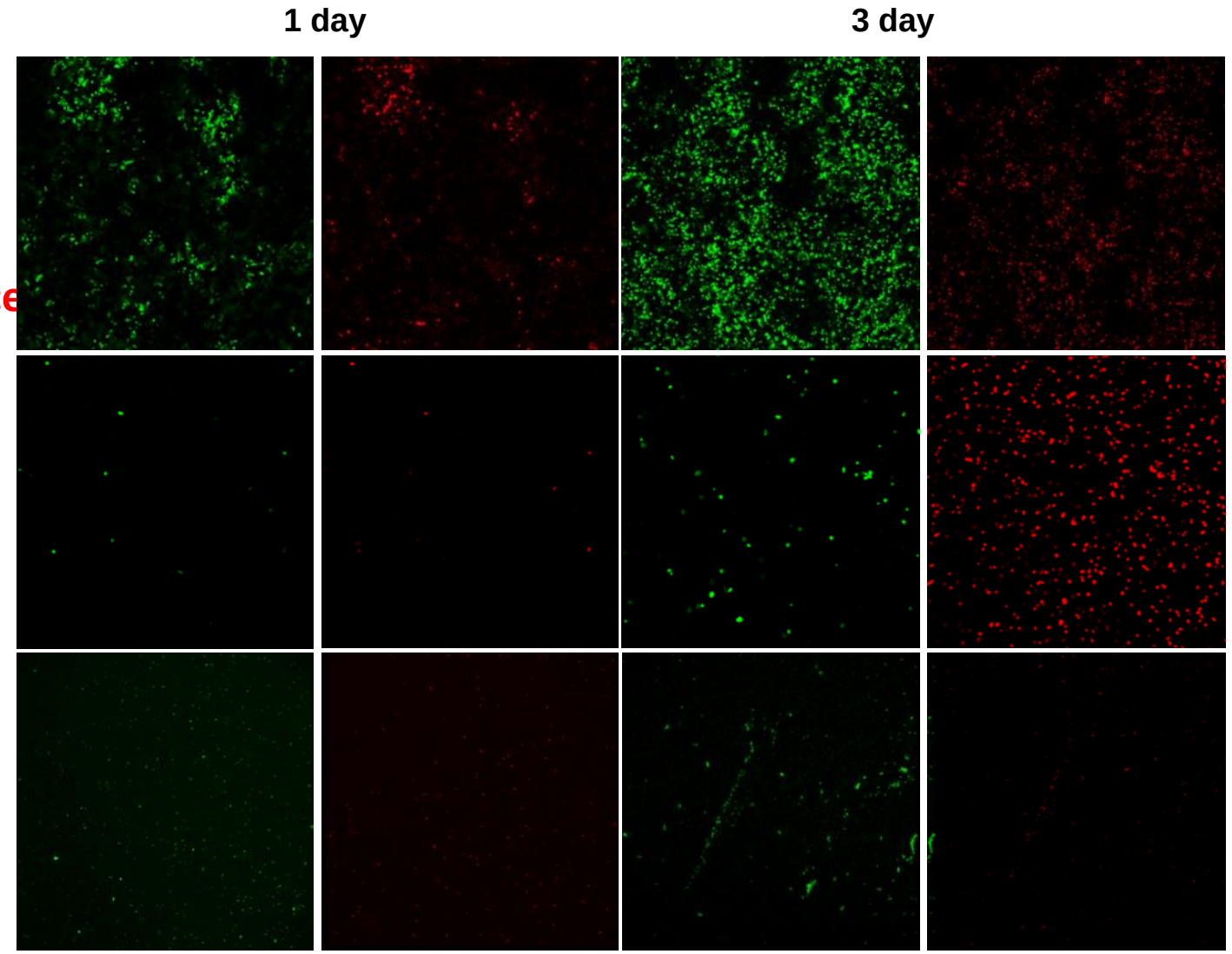
☐ The nanosilver surface showed the highest cytotoxicity, while the cytotoxicity was decreased for superhydrophobic surface because of the release inhibition of Ag^{+}.

Antibacterial mechanism of SS surface



- The superhydrophobic surface separated the surface and the medium in initial immersing stage, reduced the adhesion of the biofilm, and inhibited the release of Ag^+.
- The superhydrophobic surface and released Ag^+ ions synergistically mitigated the biofilm.

Antibacterial superhydrophilic surface



S. aureus

Conclusion:

- A superhydrophobic (hydrophilic) surface was constructed on the surface of 316L stainless steel by self-assembly of polydopamine, nano-silver particles and PFDT.

- Biofilm was synergistically inhibited by the superhydrophobic surface and the released silver ions.

- The superhydrophilic surface also exhibited strong anti-biofilm ability.

Acknowledgment

- Prof. Tingyue Gu (Ohio University)
- Prof. Fuhui Wang (Northeastern University, China)
- Prof. Xiaogang Li (University of Science and Technology Beijing)
- Prof. Ke Yang (Institute of Metal Research, Chinese Academy of Sciences)
- Prof. Dawei Zhang (University of Science and Technology Beijing)
- Prof. Chengying Jiang (Institute of Microbiology, Chinese Academy of Sciences)
- Prof. Hao Song (Tianjing University)

All my graduate students and my family members!!!

Acknowledgment

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- **Northeastern University , China**