SELF-HEALING COATINGS WITH MULTI-LEVEL PROTECTION BASED ON ACTIVE NANOCONTAINERS

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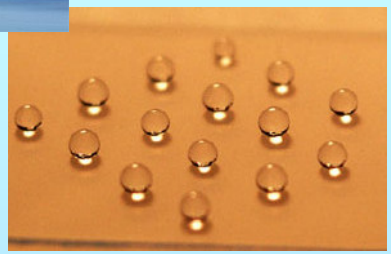
Protective coatings on metallic substrates

+Aesthetic properties
+Tailored surface properties
+Good barrier against corrosive species

-Lack of self-healing



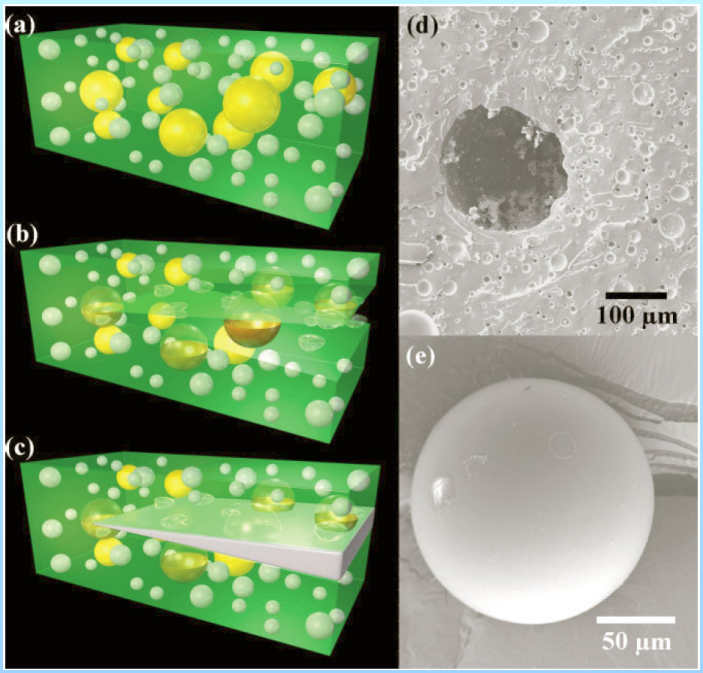
Passive + active

Coating + Active Healing Agent

+Combination of barrier and self-healing

Definition of Self-Healing

The term "self-healing" in materials science means self-recovery of the mechanical integrity and initial properties of the material after destructive actions of external environment or under influence of internal stresses.



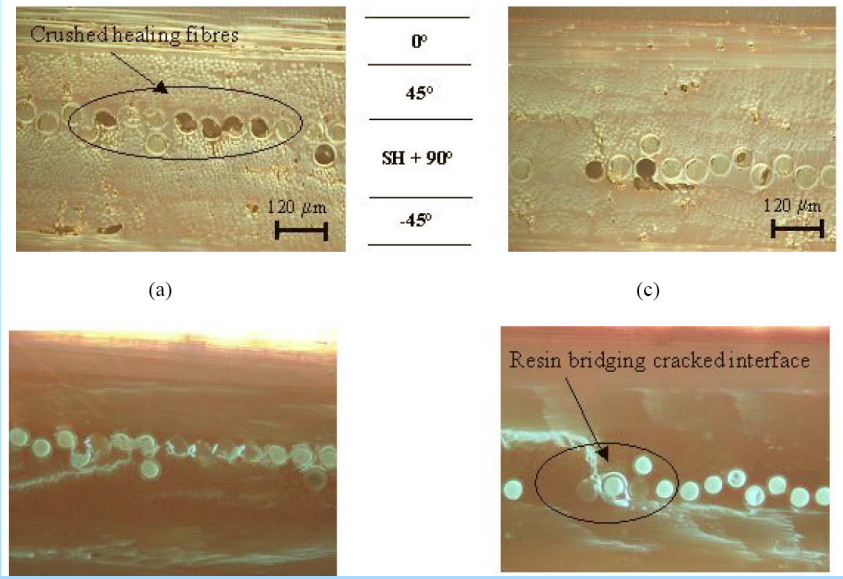
Self-healing composite consisting:

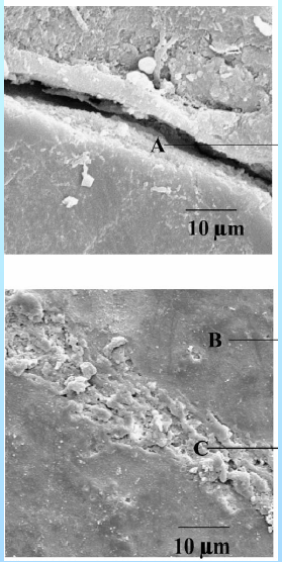
- **microencapsulated catalyst (yellow)**
- **phase-separated healing-agent droplets (white)**
- **dispersed in a matrix (green);**

B.S.H. Cho, H.M. Andersson, S.R. White, N.R. Sottos, P.V. Braun, *Adv. Mater.* **2006*, 18,***997-1000.

Self-Healing Protective Coatings

The classical understanding of self-healing is based on the complete recovery of the coating functionalities due to a real healing of the defect retrieving initial coating integrity.





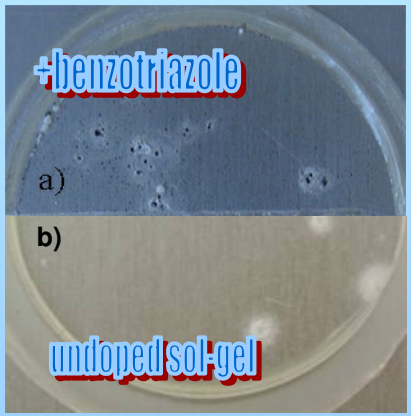
The hindering of the corrosion activity in the defect by the coating itself employing any mechanisms can be already considered as self-healing, because the corrosion protective system recovers its main function, namely the corrosion protection, after being damaged.

•R.S. Trask, G.J. Williams, I.P.Bond, *J. R. Soc. Interface.* 2007, *4*,363-371.
•T. Sugama, K. Gawlik, *Mater. Lett.* 2003, *57*,4282-4290.

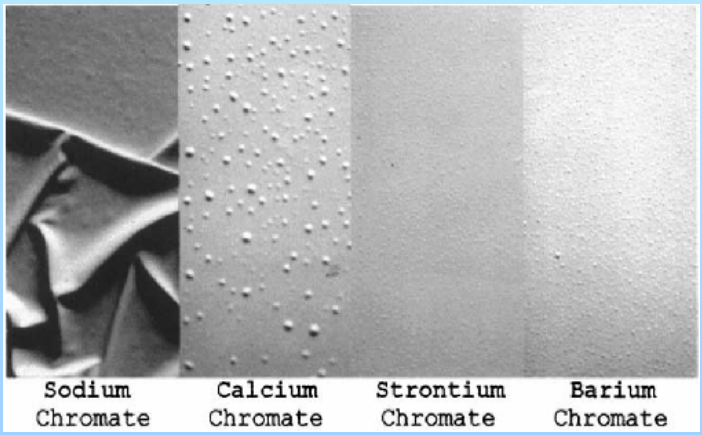
Immobilization of Healing Agents

Active agent must be encapsulated in order to prevent its interaction with components of coatings!!!

Examples of negative effect of active agents



Lower hydrolytical stability

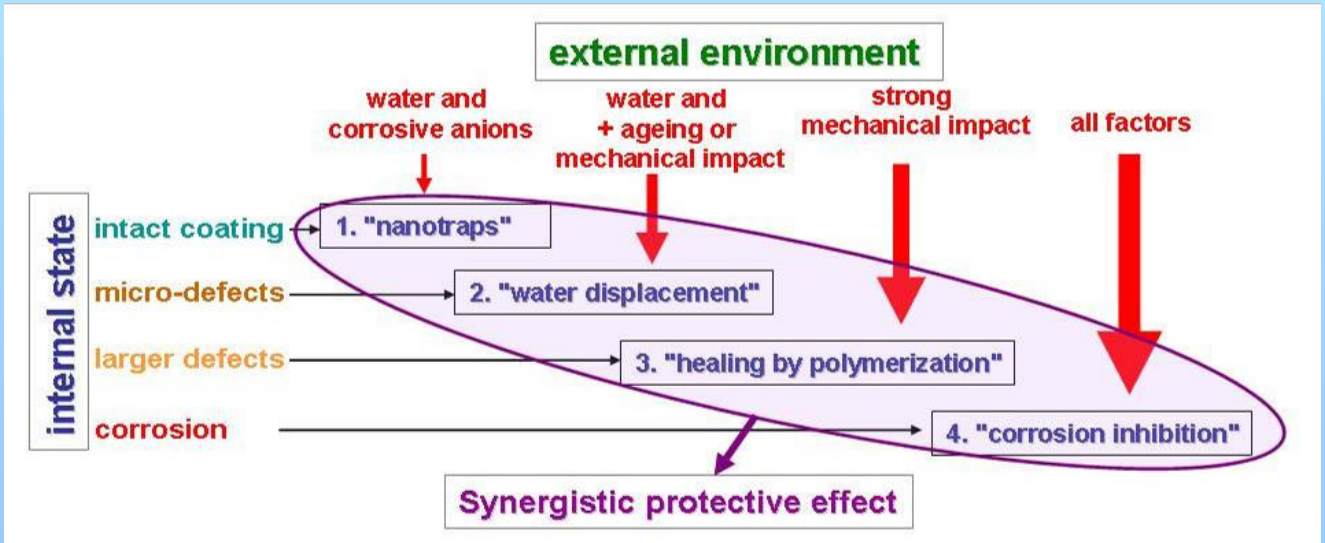


Osmotic blistering

New approach

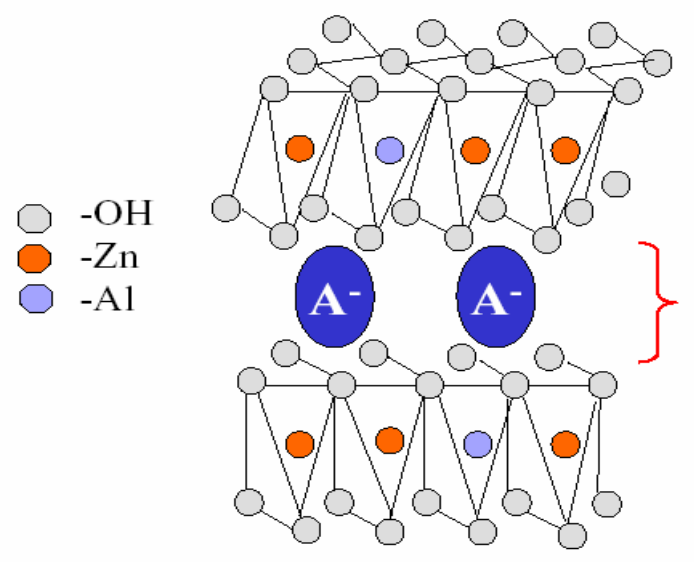
MULTI-LEVEL ACTIVE PROTECTION

- Active feed-back of the coatings depends on the internal state of the coating system and the external environmental conditions
- Different levels of active protection are working as response to different impacts



1st and 4th level: ion entrapment + corrosion inhibition

LDH pigments



Zn-Al layered double hydroxide (LDH) powders

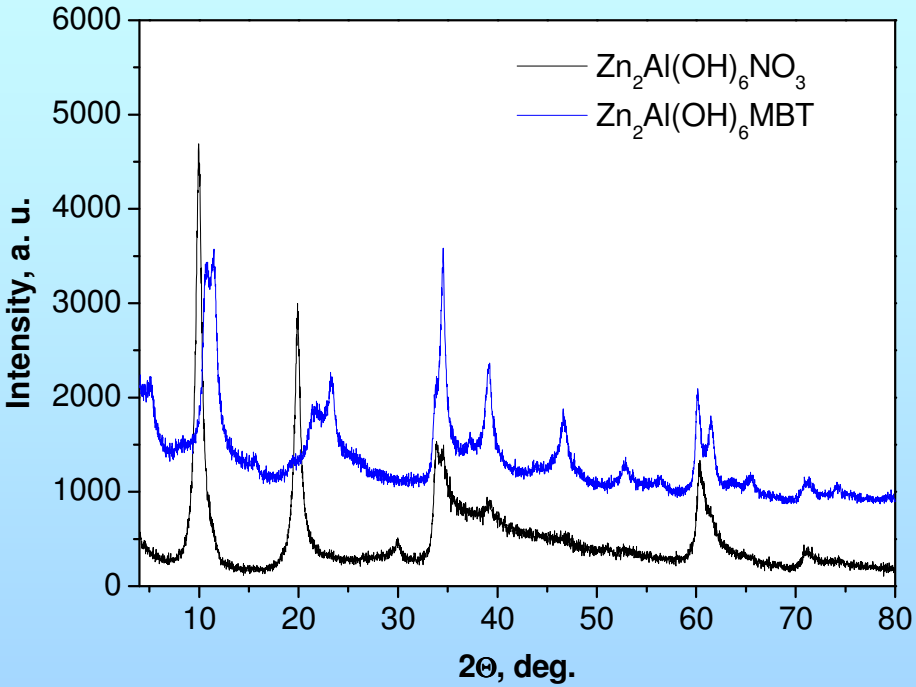
Inhibiting anions:

- **Mercaptobenzothiazole (MBT)**
- **vanadate**

Two ways of pigment preparation:

- **direct synthesis (-formation of insoluble salts);**
- **ion-exchange**

Zn-Al LDH pigments

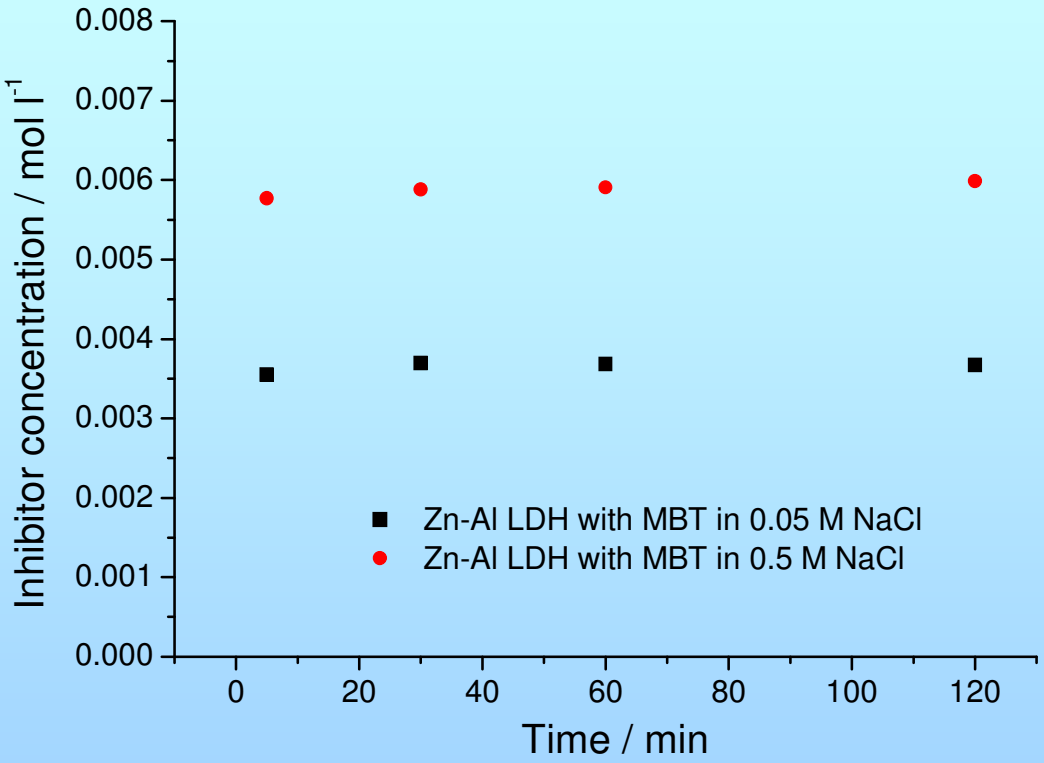


d(003)

$Zn_2Al(OH)_6NO_3$ - 0.8892 nm

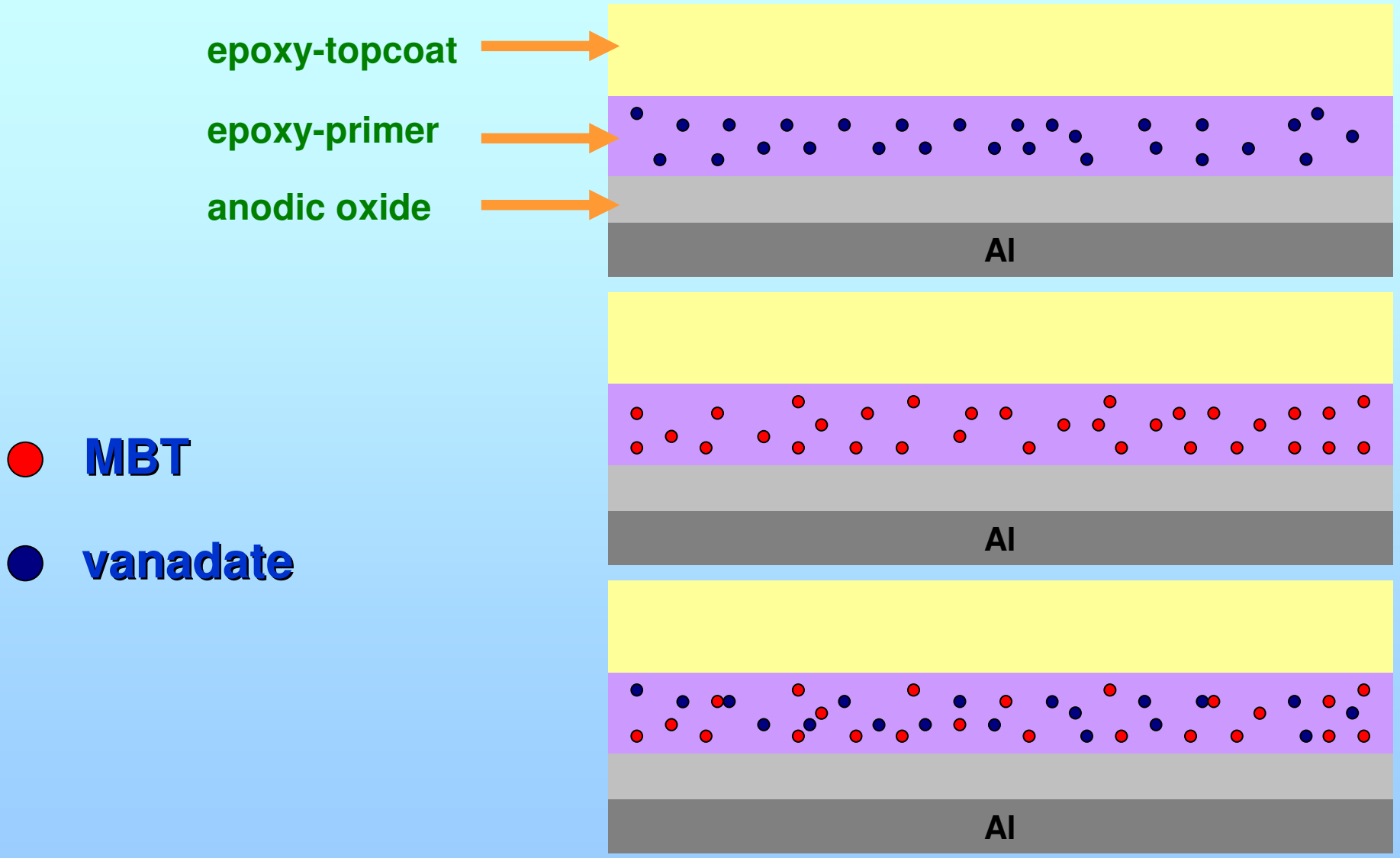
$Zn_2Al(OH)_6MBT$ - 1.71 nm

Release of inhibitors from LDH pigments



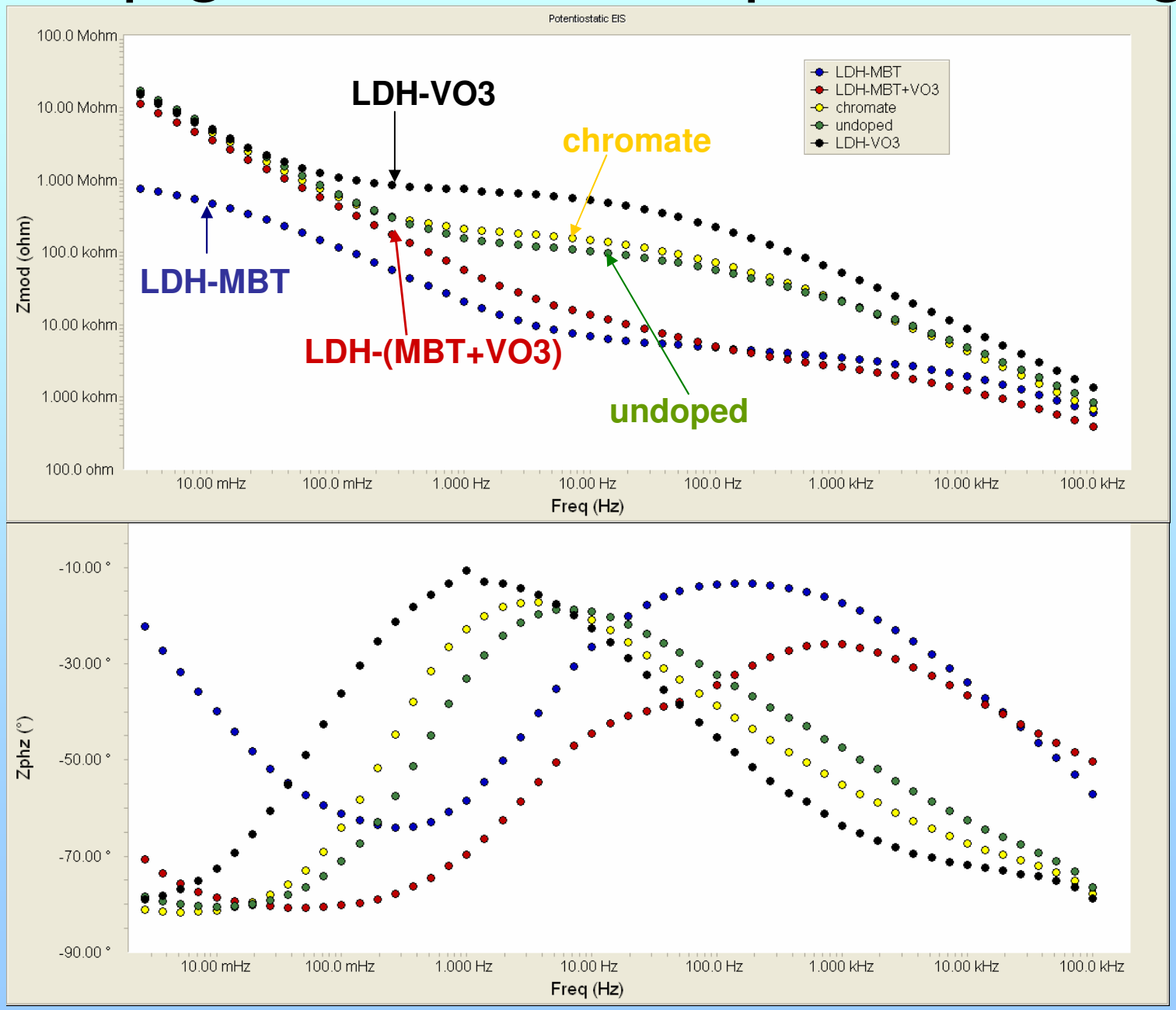
- **LDH pigments demonstrate fast release-response**
- **Release of inhibitor is triggered by chloride ions**

LDH pigments in aerospace coatings



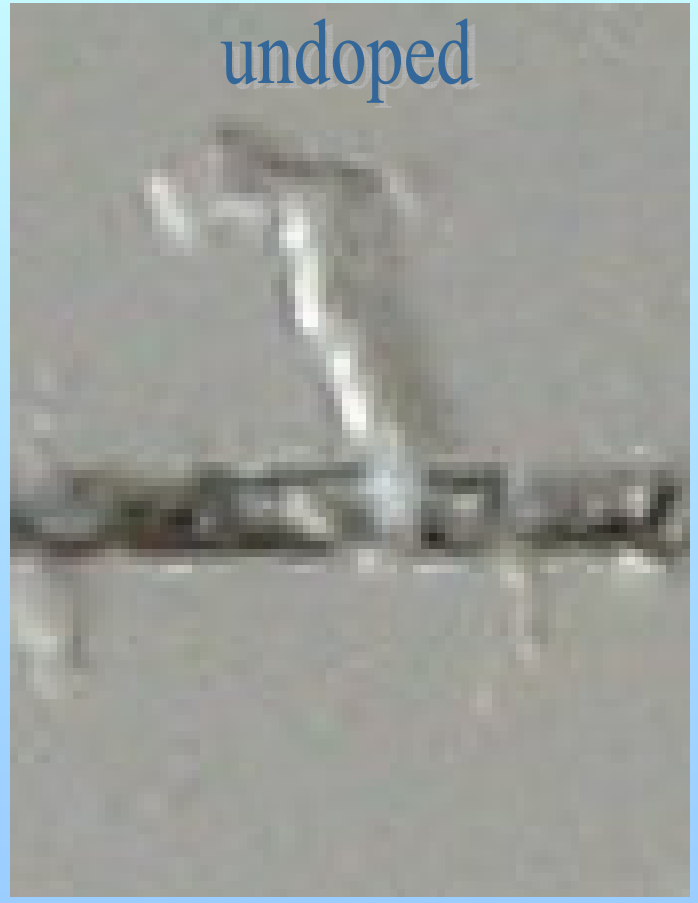
LDH pigments in aerospace coatings

2 months in 0.5 M NaCl

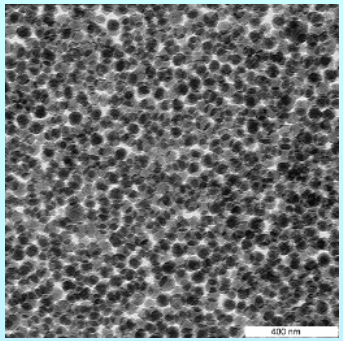


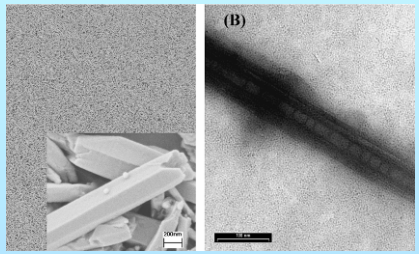
LDH pigments in aerospace coatings

960 h of filiform corrosion tests



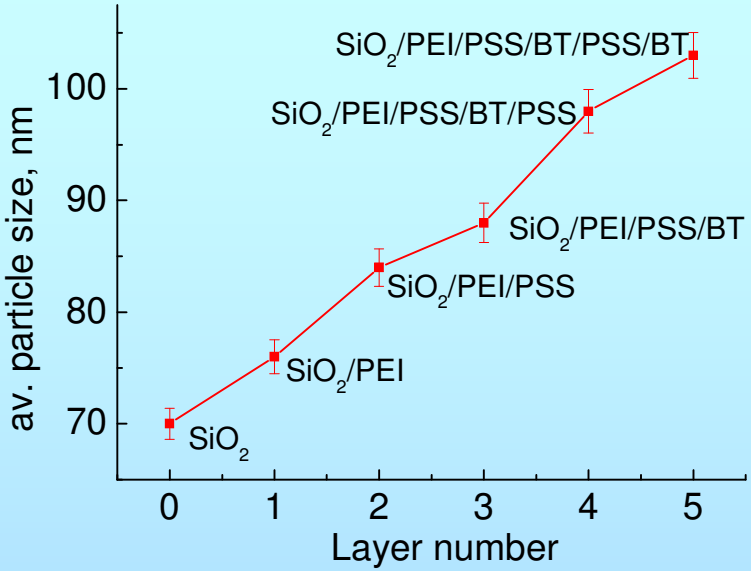
LbL polyelectrolyte shells

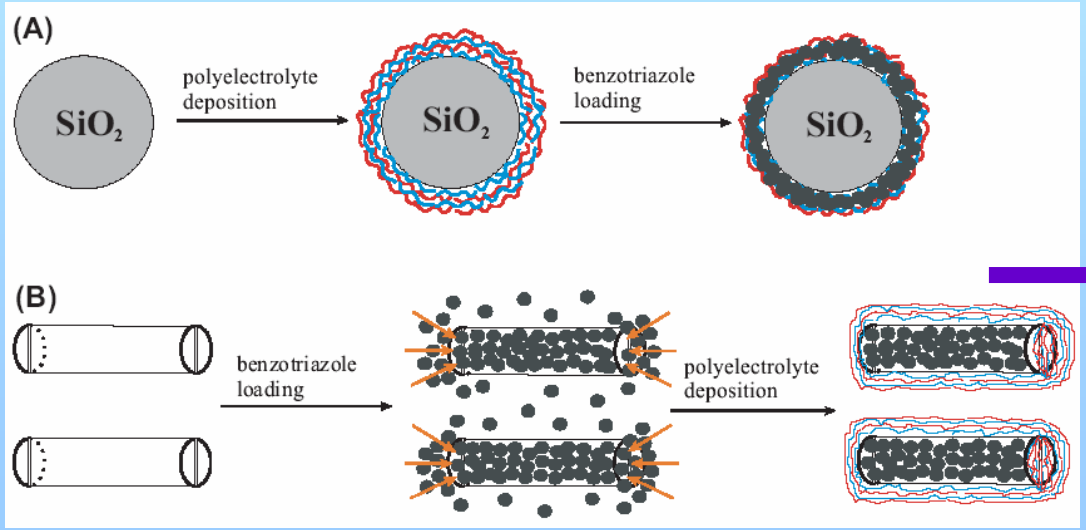


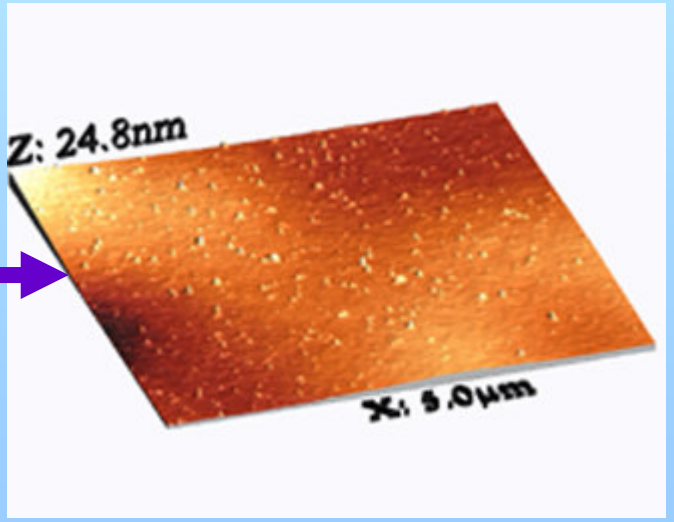


Layer by Layer

assembling process

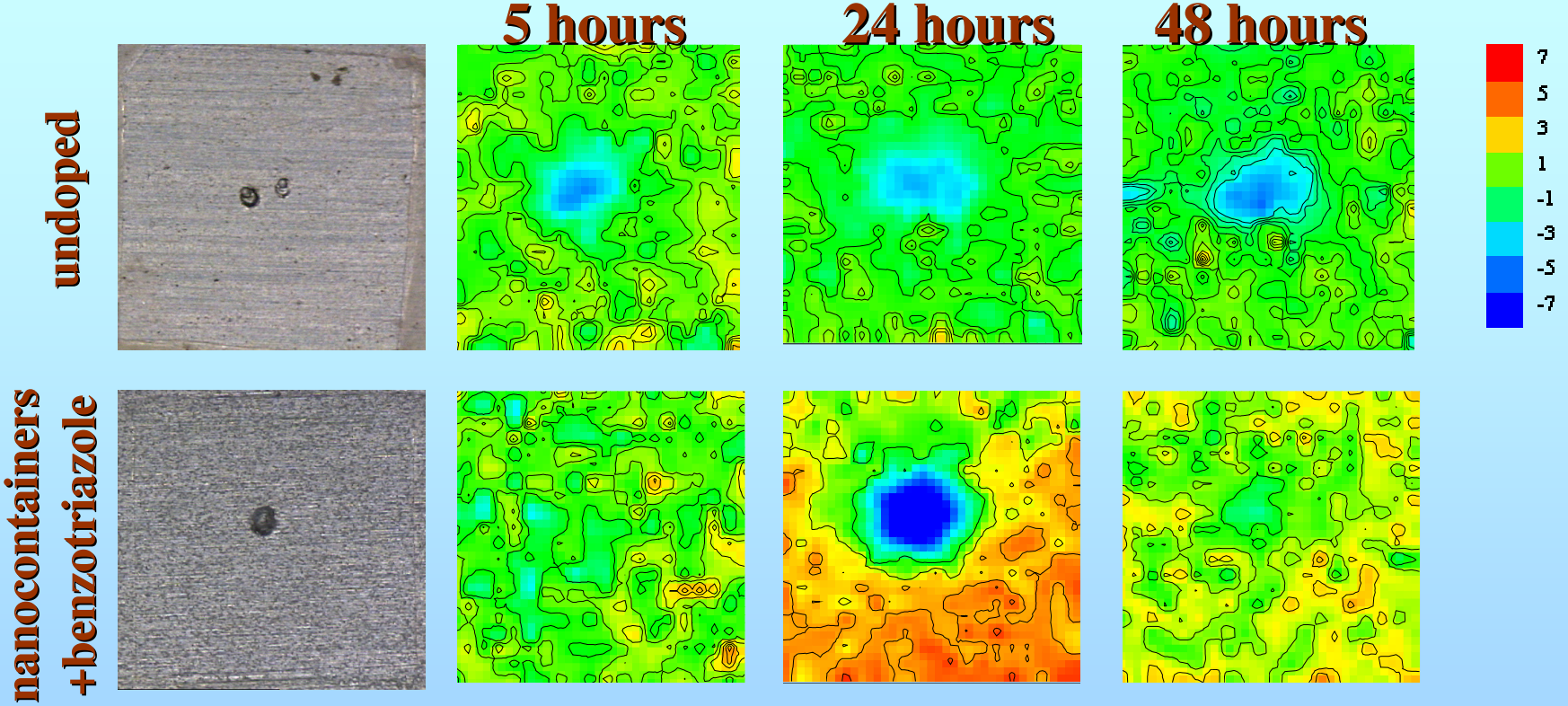






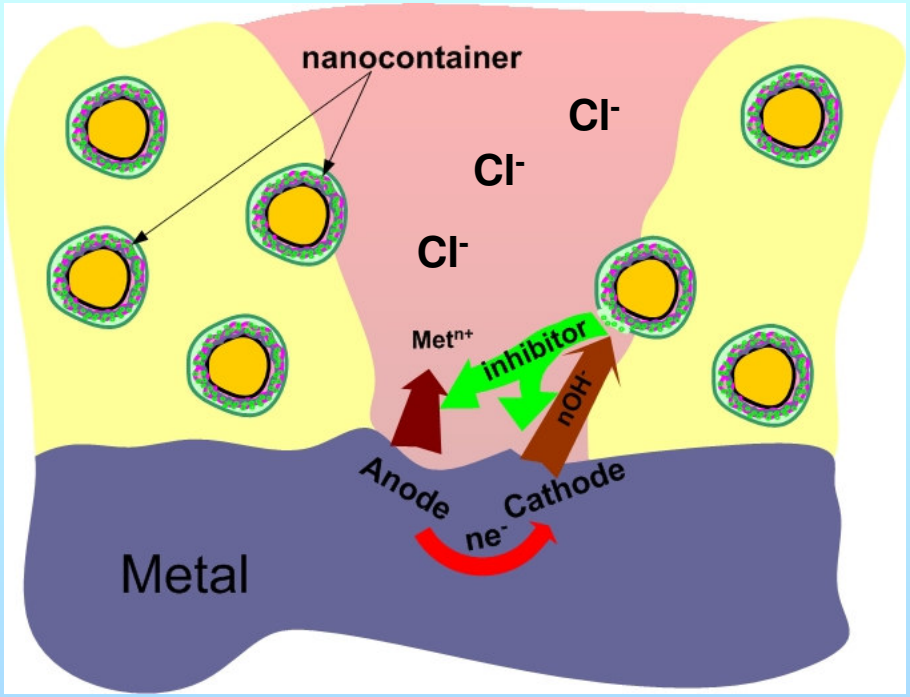
Self-healing of an artificial defect

SVET maps



Suppression of the active corrosion processes demonstrates self-healing of artificial defect in sol-gel film doped with nanocontainers loaded with benzotriazole

Mechanism of "smart" self-healing



Appearance of defect opens pathway for chloride ions

Corrosion processes start on the alloy surface

Cathodic reactions generate hydroxyls leading to local increase of pH:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \uparrow$$

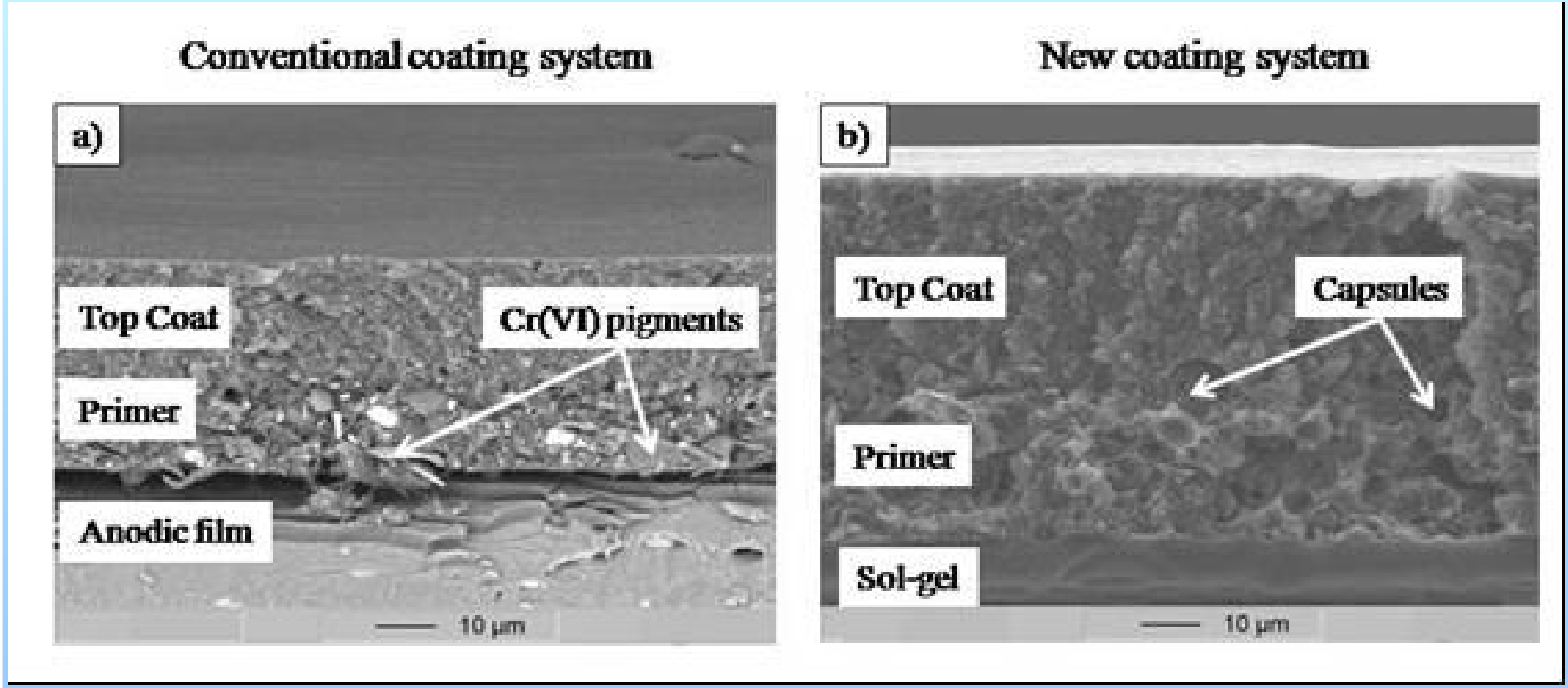
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Raise of pH increases permeability of polyelectrolyte shell leading to release of inhibitor

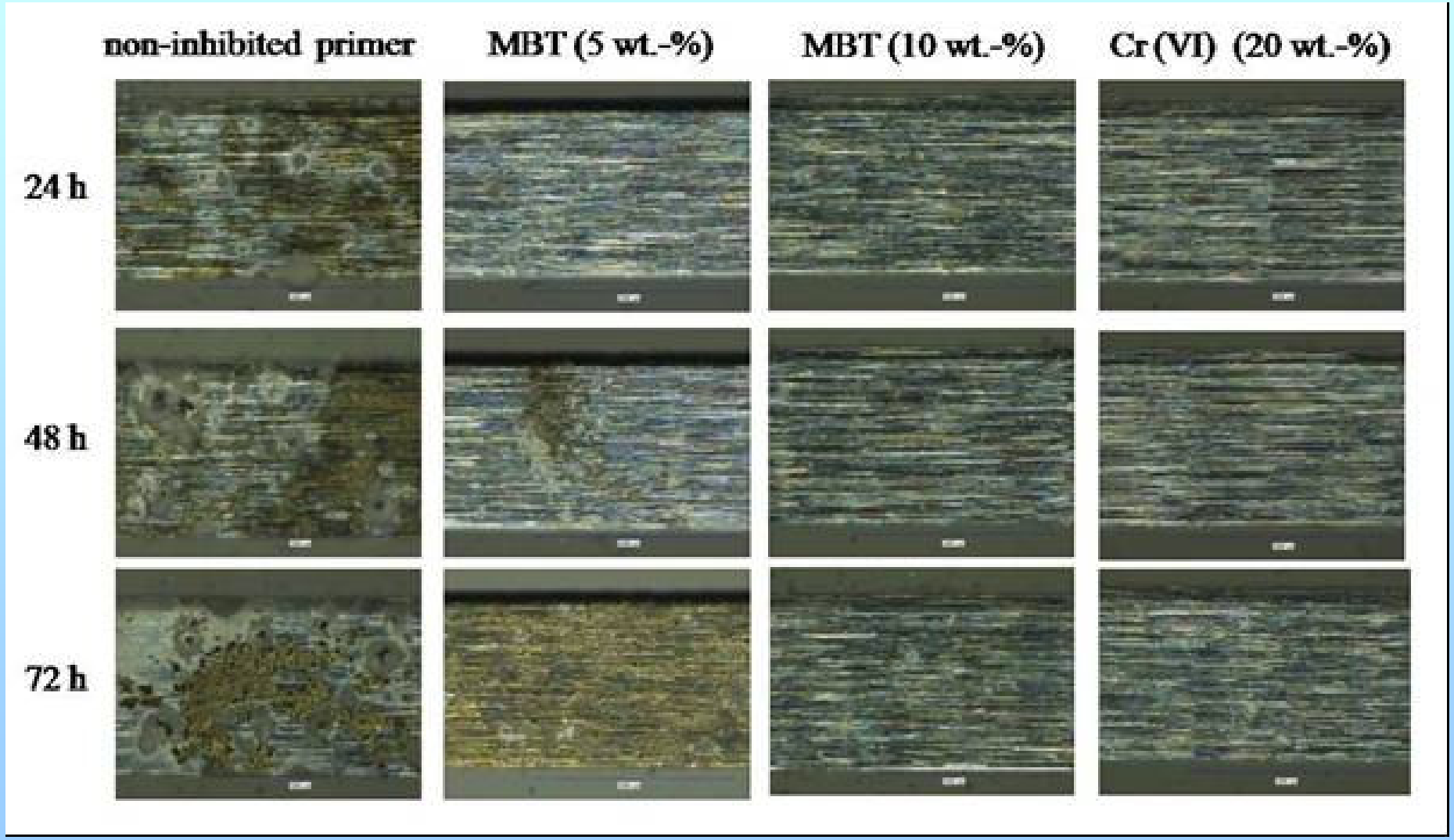
Released benzotriazole hinders corrosion activity healing the defect

2nd and 4th level: water displacement + corrosion inhibition

Capsules of water displacing agent (diisopropylnaphthaline) and corrosion inhibitor (MBT) produced by microemulsion interfacial polymerization.



Self-healing of defects (2nd + 4th levels)



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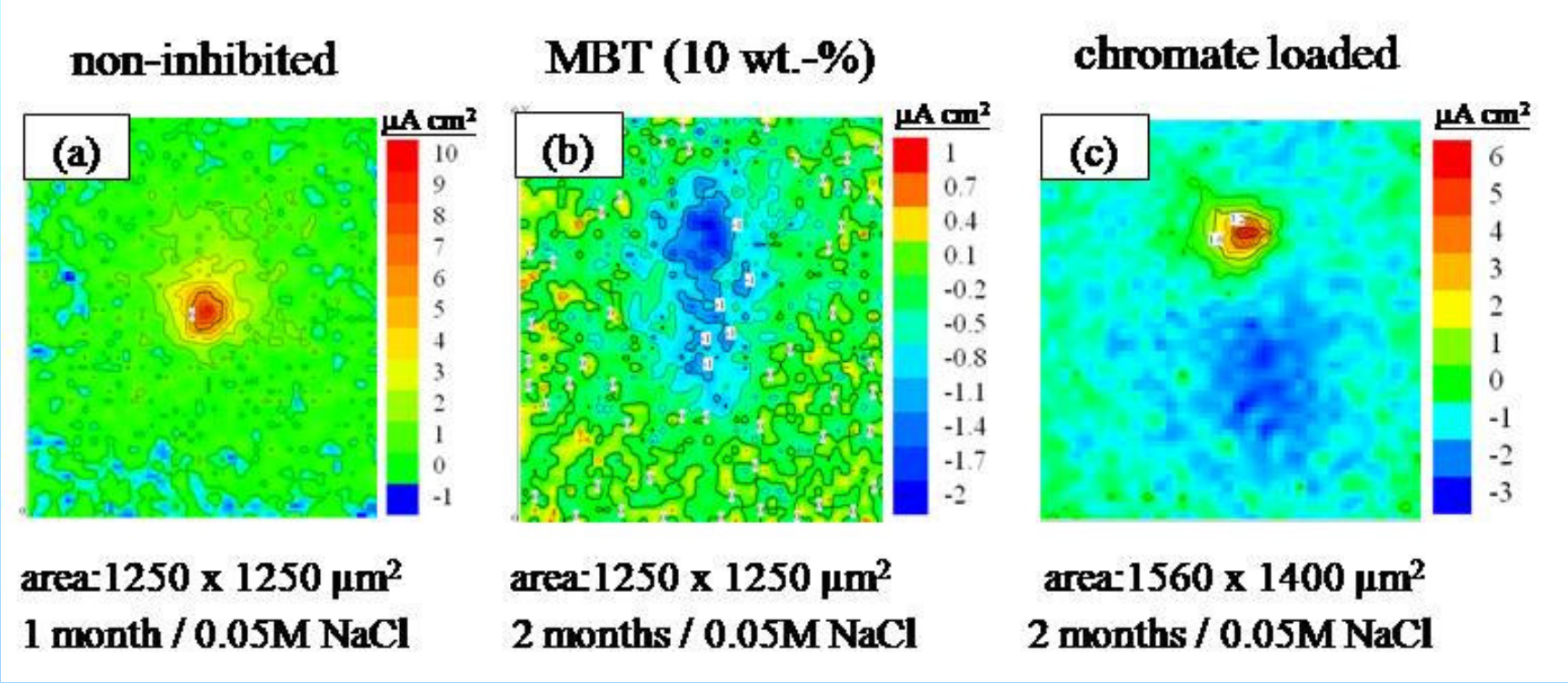

Conclusions

- ✓ *New concept of multilevel anticorrosion system based on active nanocontainers for protective coatings is proposed;*
- ✓ *Nanocontainers of corrosion inhibitors based on LDH nanopigments are developed demonstrating effective corrosion protection and self-healing ability;*
- ✓ *“Smart” nanoreservoirs of corrosion inhibitors are also produced using polyelectrolyte shells assembled by LbL approach. This containers are pH-sensitive providing release of corrosion inhibitor on demand;*
- ✓ *Capsules of water displacer and corrosion inhibitor are produced by microemulsion polymerization. Coatings doped with these capsules demonstrate superior corrosion protection performance.*

Acknowledgements

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Thank you for attention!