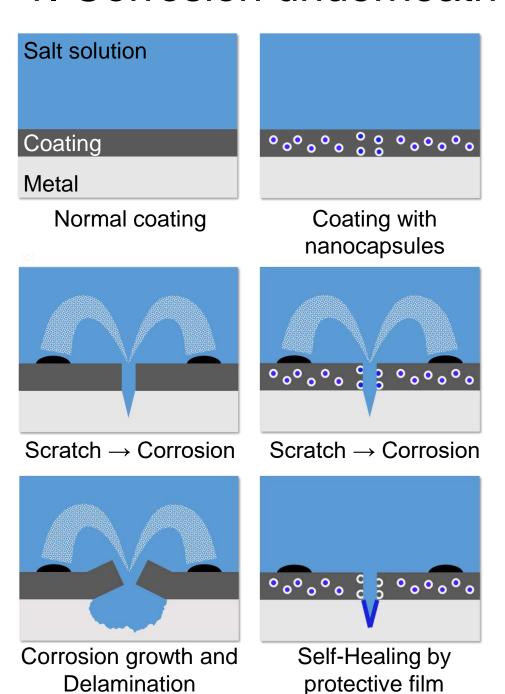


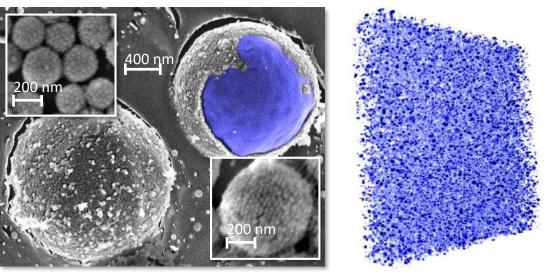
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1. Corrosion underneath scratched coatings



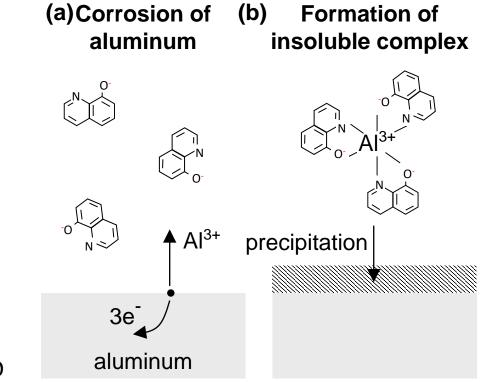
At US \$2.2 trillion, the annual cost of corrosion worldwide is over 3% of the world's GDP. Protecting metals from corrosion is achieved with polymeric most efficiently coatings. However, most coatings require the use of organic solvents with negative impact on the health of workers and the environment. Waterborne coatings are environmentally friendly alternatives but show poorer anticorrosive performance. We develop "smart water-borne coatings" with enhanced anticorrosive properties based on corrosion inhibitor filled nanocapsules.

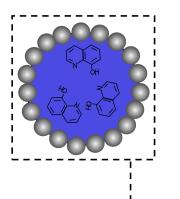


Capsules of different size Capsule distribution in 3D

2. Corrosion inhibitor and capsules

Pitting-corrosion of aluminum releases Al3+ ions into water (see (a)). The corrosion inhibitor 8HQ forms a water insoluble complex with Al³⁺ that precipitates on the aluminum surface (b). The precipitate forms a passivation layer on the aluminum, preventing further corrosion.





Here, we investigate nanoparticle stabilized emulsion droplets for the encapsulation of 8HQ. The capsules are embedded in a protective barrier coating aluminum. Upon on scratching the coating, self-healing of

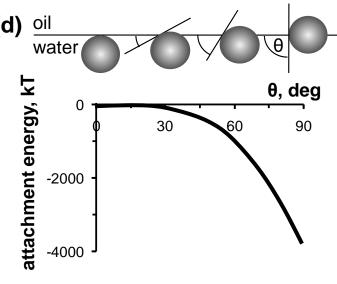
> the exposed metal surface by release of 8HQ takes place. objective is to develop an anticorrosive system with the following features:

- Inexpensive/scalable capsule fabrication
- Multifunctionality of capsule building blocks
- Adjustable capsule size (Nano- and microcapsules to be used in very thin and thick coatings)
- Substitution of solvent- with water-borne coatings
- No use of cancerogenous corrosion inhibitors such as hexavalent chromates

2. Interfacial attachment of nanoparticles

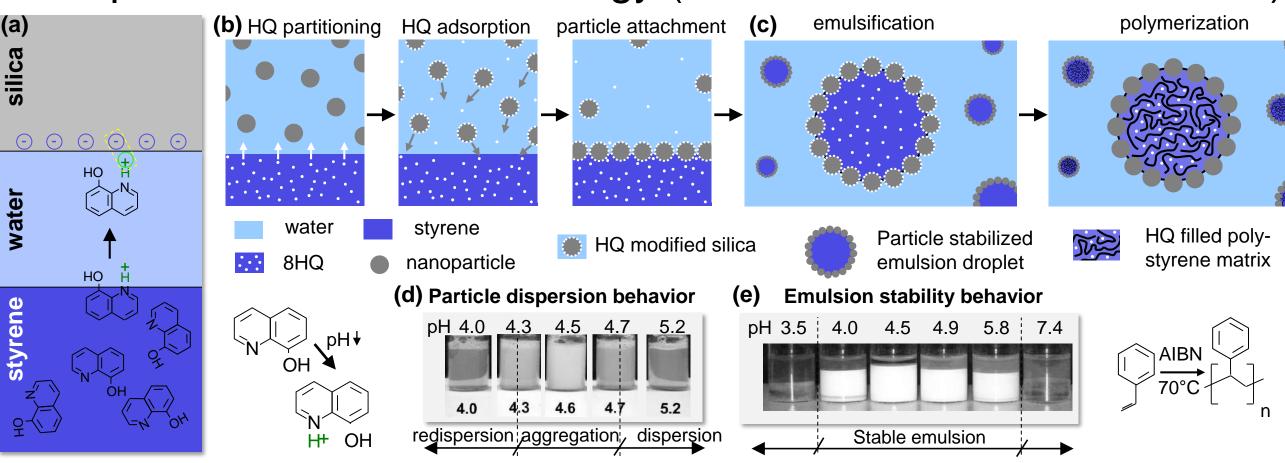


We use silica nanoparticles as building blocks for the capsules (SEM) image in (a)). Silica is naturally hydrophilic but can become partially hydrophobic upon surface modification. We alter the hydrophobicity of silica by the adsorption of positively charged 8HQ on the negatively charged silica particles (b). After this modification the particles attach



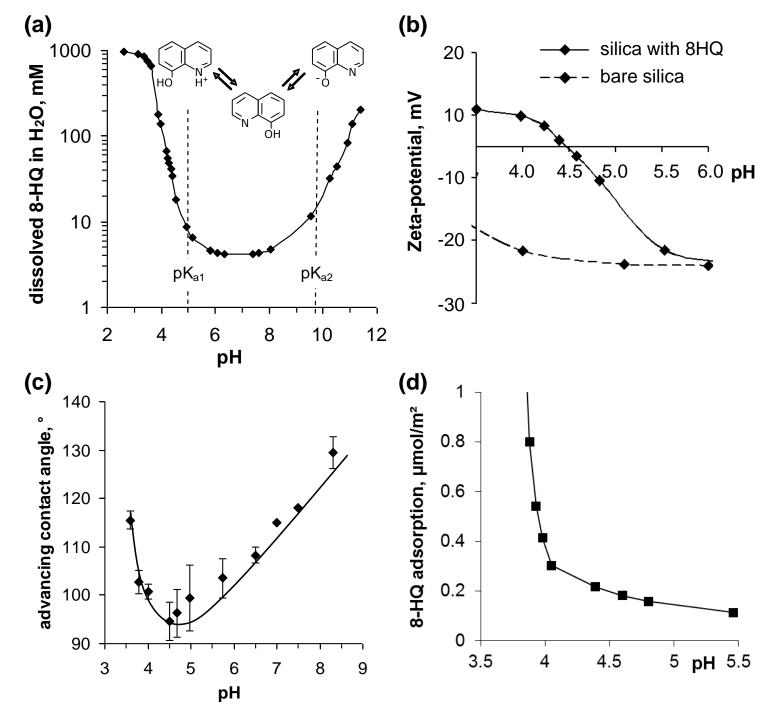
to oil/water interfaces as shown in (c). The more 8HQ adsorbs on the particles, the stronger the particles attach to the oil water interface. This process can be described theoretically with the contact angle θ and the attachment energy (d). Practically, the particles attach irreversibly for attachment energies > 100kT.

3. Capsule fabrication technology (8-HQ as bifunctional molecule)

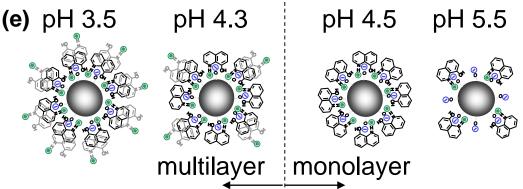


We dissolve large amounts of 8HQ in oil (up to 50% in styrene). By reducing the pH of the surrounding water, small amounts of the 8HQ dissolve in water and become positively charged and adsorb on the particles (a). This causes the particles to attach to the styrene/water interface (b). Upon emulsifying particle stabilized droplets are formed that can be polymerized to obtain 8HQ filled polymer/silica composite capsules (c). The pH value determines the amount of positively charged 8HQ in the water. Interestingly we find that the particles aggregate at pH 4.5, but can be suspended again below pH 4 (d). Analogously, the emulsion shows a narrow stability window between pH 6 – pH 4 (e).

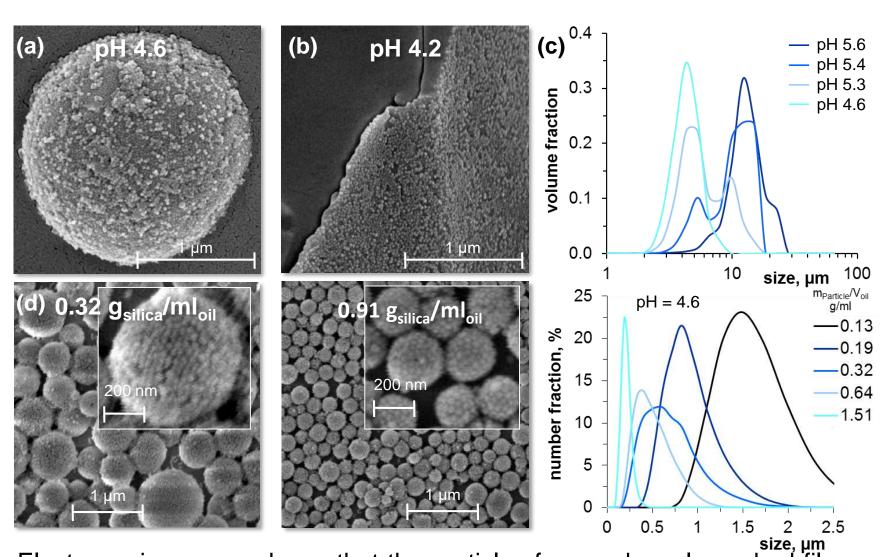
4. Physical chemistry of particle surface modification



How can the unusual particle and emulsion stability be explained? (a) Shows the increase of 8HQ solubility in water by orders of magnitude upon decreasing the pH. Simultaneously, the surface charge of the nanoparticles decreases upon adsorption and becomes positive at pH 4.5 (b). The contact angle changes accordingly, indicating the particle attachment to the oil/ water interface (c). Surprisingly, we find that adsorption of 8HQ increases dramatically below pH 4.0 (d), indicating the formation of multilayers of 8HQ on the silica (e). The 8HQ multilayers make the silica hydrophilic again and explain the unstable emulsions below pH 4.

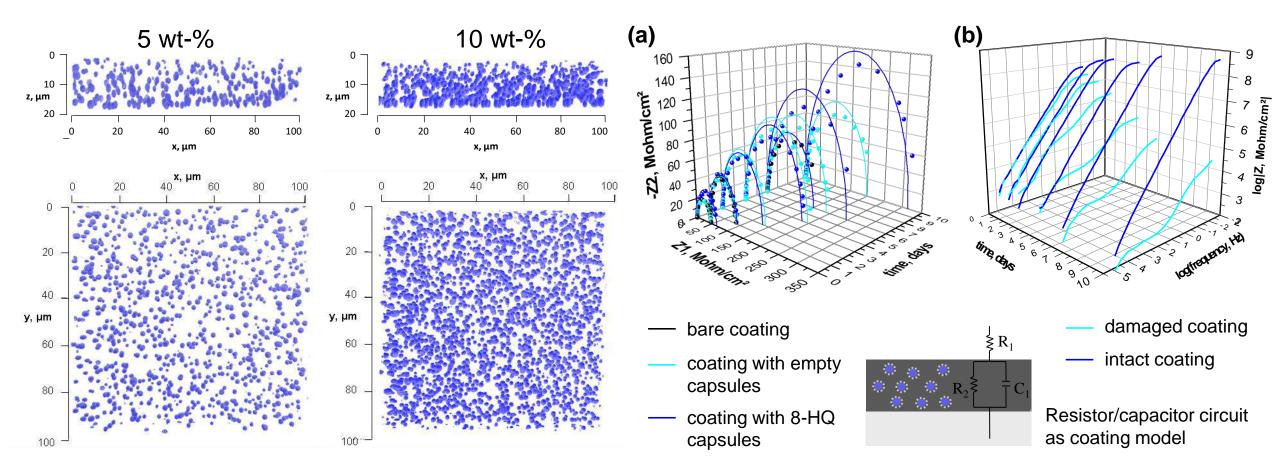


5. Particle stabilized droplets with 8HQ-silica



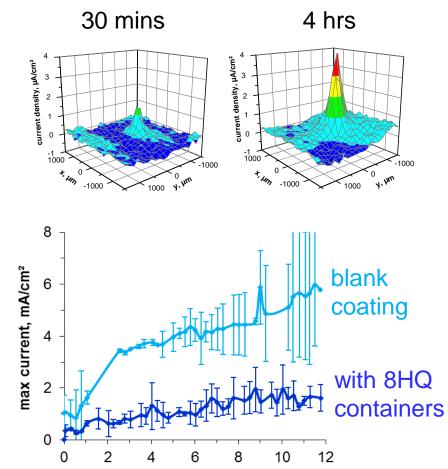
Electron microscopy shows that the particles form a densely packed film on the droplets at pH 4.6 (a). However, at pH 4.2 the particle packing density is decreased (b). Decreasing the pH from 6 to 4.5 decreases the droplet size to a few µm (c). However, the addition of a hydrophobic co-stabilizer allows us to further decrease the droplet size down to only 200 nm (d).

6. Capsule distribution in coating 7. Anticorrosive properties of the coating



The capsules are introduced into a water-borne alkyd coating and coated on an aluminum substrate. Confocal Laser Scanning Microscopy shows that the capsules are well distributed in the coating and no aggregates are present. Up to 25 wt-% of capsules can be embedded in the coating without introducing defects.

Electrochemical impedance spectroscopy shows that the unscratched coatings have excellent corrosion resistance. Coatings with 8HQ capsules have superior corrosion resistance than bare coatings as indicated by the larger semicircles in (a). On the other hand, coatings with defects show decay over time (b).



Scanning vibrational electrode measurements show that scratched coatings with 8HQ capsules have a decreased corrosion activity compared to bare coatings indicating self-healing ability.

8. Conclusion

A novel method for the encapsulation of organic active agents in nanoparticle-armored polymer composite nanocontainers (analog of Pickering emulsions) is introduced. The multifunctionality of the constituents allows a fabrication path that does auxiliary materials. require Embedding the composite nanocontainers into a water-based alkyd resin and subsequent film formation yields a homogeneous polymer film doped with highly disperse composite nanocontainers. The resistance and self-healing of such a film on aluminium is enhanced.

Publications from this work:

- M.F. Haase, et al., Advanced Materials, 2012, 24, 18, 2429
- M.F. Haase, et al., Journal of Physical Chemistry C, 2010 114, 17304
- M.F. Haase, PhD thesis, University of Potsdam, 2011, Modification of Nanoparticle Surfaces for Emulsion Stabilization and Encapsulation of Active Molecules for Anti-Corrosive Coatings,

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