Chemical functionalization of nanoparticles

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Content

Objectives

- Nanotechnology: chemical functionalization of nanoparticles
- Development of nanotechnology-based organic coating to enhance anticorrosion properties: incorporation of nanoparticles in organic coatings
- Characterization techniques of nanoparticle surface

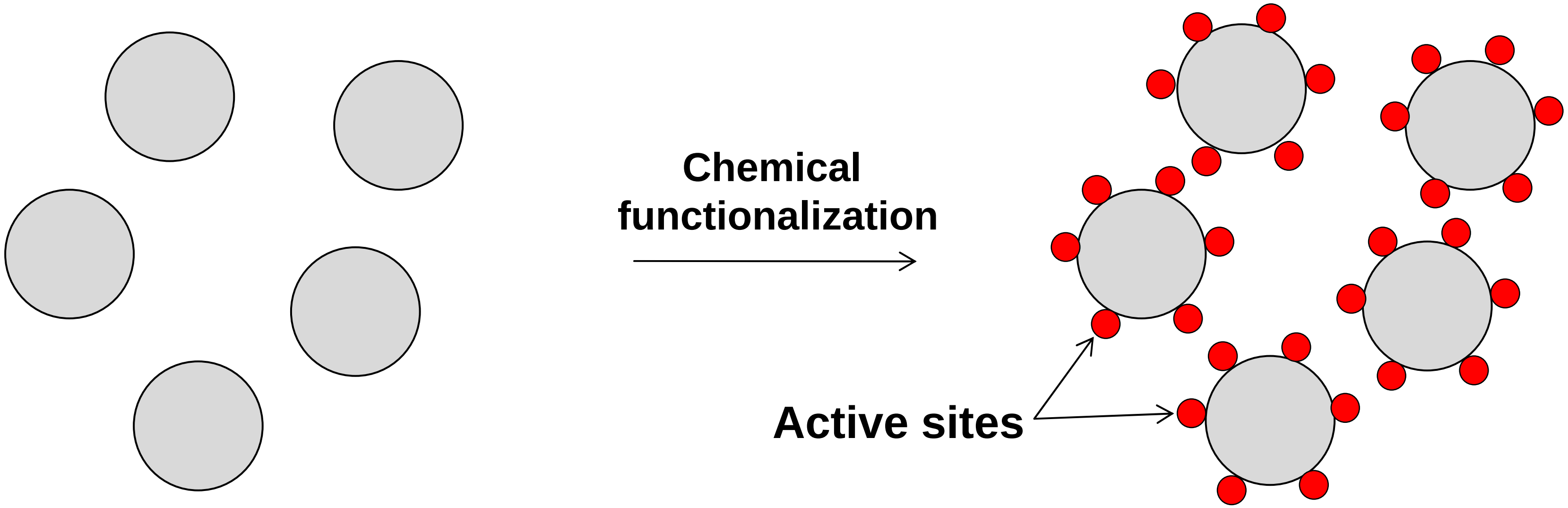
Introduction

- **Nanotechnology:** study of materials in nanometric scale (nanoparticles, nanolayers, nanocoatings) – 1 nm to 100 nm
- **Advances in this area of science:** novel phenomena (physical, chemical and biological) materials when its take on the nanoscale
- **Chemical functionalization of nanoparticles**: modification of nanoparticle surface to apply in different areas: biological, medical, engineering, etc.

Introduction

What's chemical functionalization of nanoparticle ?

Chemical modification of nanoparticle surface



Nanoparticle

Nanoparticles functionalized

Hydrophilic, hydrophobic, conductive, anticorrosive

Introduction

Development of nanotechnology-based organic coating to enhance anticorrosion properties (incorporation of nanoparticles)

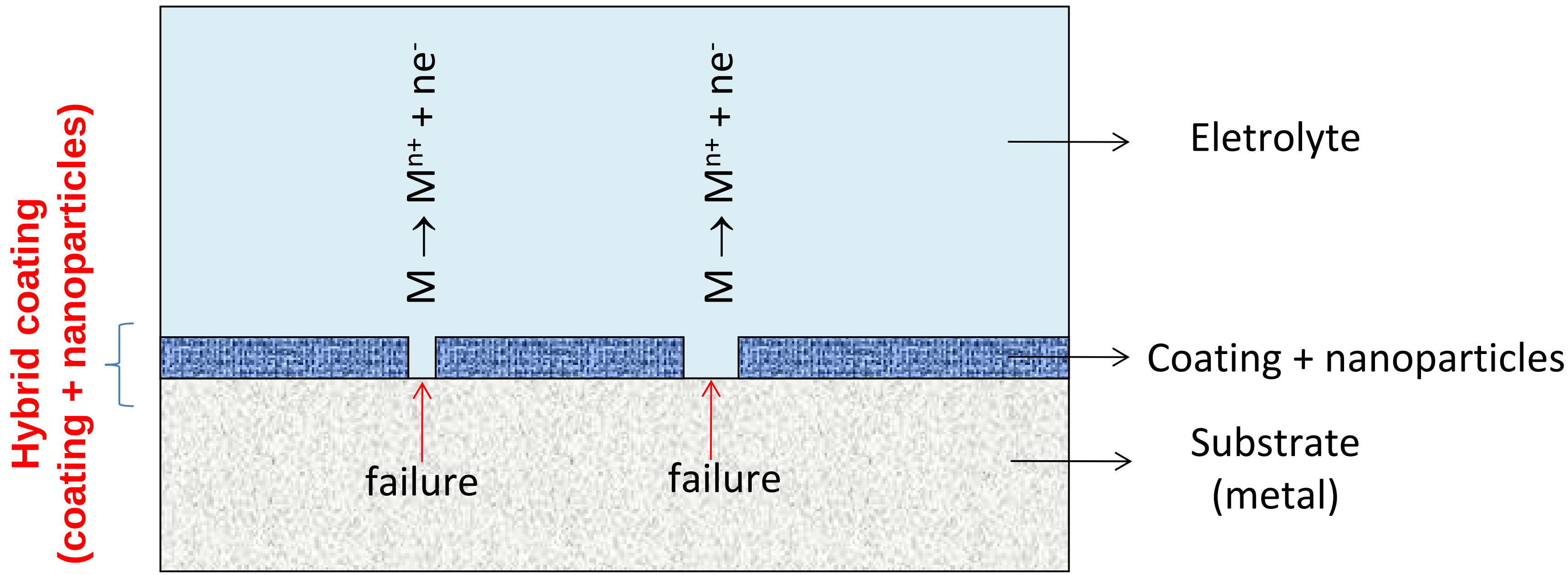
- **Corrosion:** protection of metal structures from corrosion by organic coatings is a well know practice;
- **Commercial problems:** High toxicity of some components of the coating
- With the quest for new **developed coating** systems with low toxicity and high performance

Incorporation in the coating

Nanoparticles chemically functionalized

Applications

Nanotechnology and anti-corrosion systems

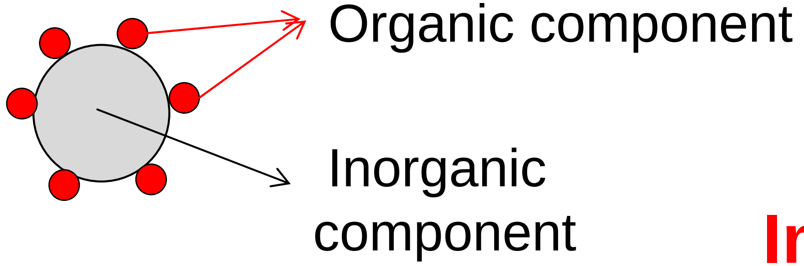


- The improvement in the properties of the nanocoatings is attributed to their nanoparticles functionalized ;
- Nanomaterials mostly used in coating system: SiO_2, TiO_2, ZnO, Al_2O_3, Fe_2O_3, nano-aluminum, nano-titanium

Multi-functional **hybrid coatings (inorganic and organic components)** for scratch and corrosion resistance:

•the **inorganic components (nanoparticle)** contribute to **increased the scratch and adhesion resistance** on metallic substrate;

•the **organic component (active site)** increase the density and **flexibility of the coating**, and enhance functional compatibility with organic paint systems



Improve coating's performance

Nanoparticles applications

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- **To improve UV-Blocking Coatings**

•Inorganic nanoparticles, as alternative to UV-blockers in coating applications

•Nano-ZnO, nano-TiO_2, nano-CeO_2 : **excellent photo- and thermal stability**

•**Example:** transparent ZnO/epoxy nanocomposite coating via in situ polymerization. Optical properties of the nanocomposite coating depends on ZnO particle size

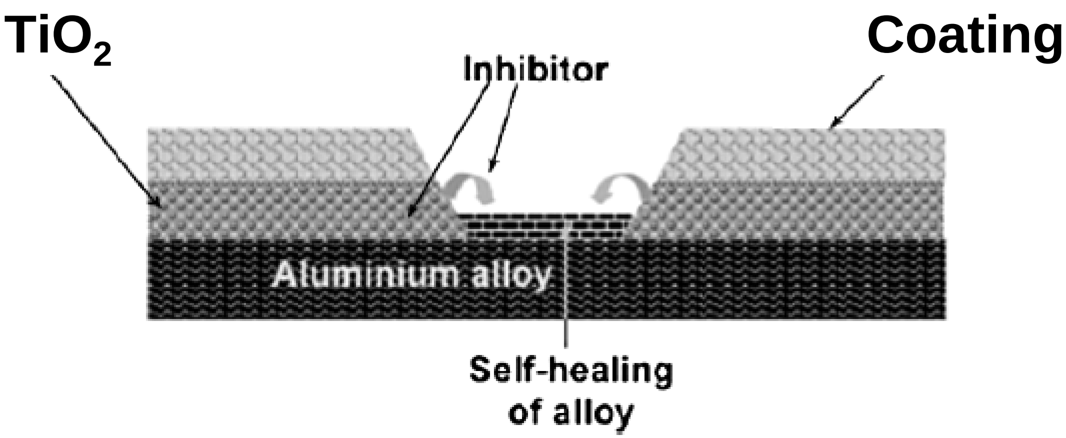
•**To develop anti-scratch and anti-abrasion coatings**

•Nano-SiO_2, nano-Al_2O_3, nano-ZrO_2 : improve the mechanical properties, increase the macro hardness, scratch resistance

Nanoparticles applications

- **To develop anticorrosive coatings**

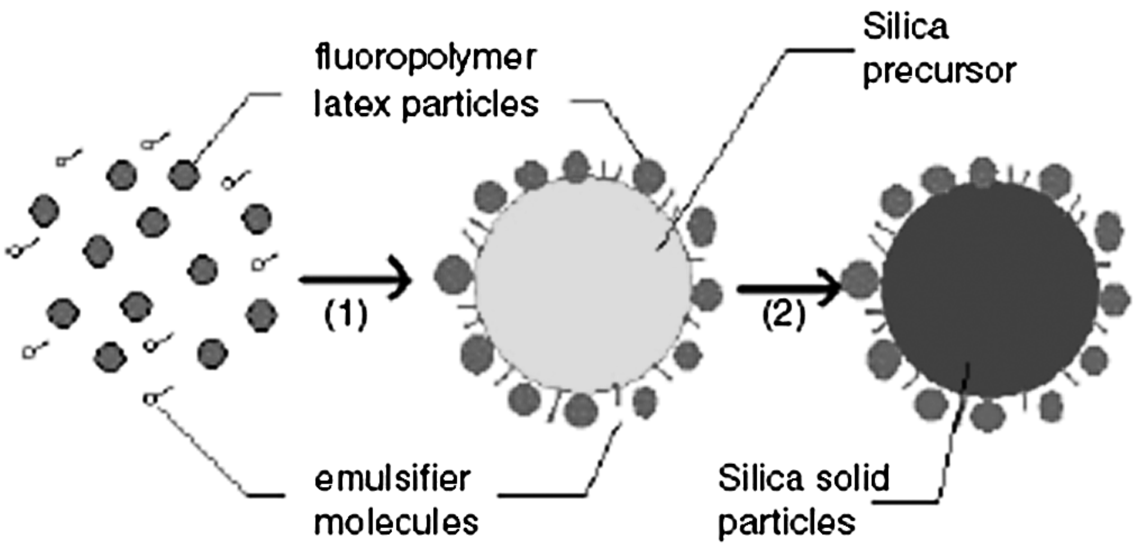
•Development of nanoporous reservoir for storing of corrosion inhibitors on the metal/coating interface (nanostructure porous **TiO_2 interlayer** prepared on the aluminum alloy surface).



Nanoparticles applications

- **To develop Super-Hydrophobic coatings**

•Continuous demand for water-repellent or hydrophobic coatings in industry



Nanotechnology application for corrosion problems

- **To develop SMART NANOCAPSULES containing inhibitors for corrosion protection**
- Corrosion inhibitors are used extensively to prevent corrosion such as **azoles group**, **amines** and **amino acids**

Example: **benzotriazole** (BTA) is one of the most effective inhibitors for corrosion of copper and its alloys

- Copper surface is covered by a film identified as [Cu(I)BTA] complex

Corrosion Inhibition Techniques → **require** → Maintaining a specific concentration of inhibiting reagent in the solution

Changes in the system
- pH
- temperature
- agitation rate

Development of SMART NANOCAPSULES → Maintaining a specific concentration of inhibiting reagent in the solution

Nanosilica applications for corrosion problems

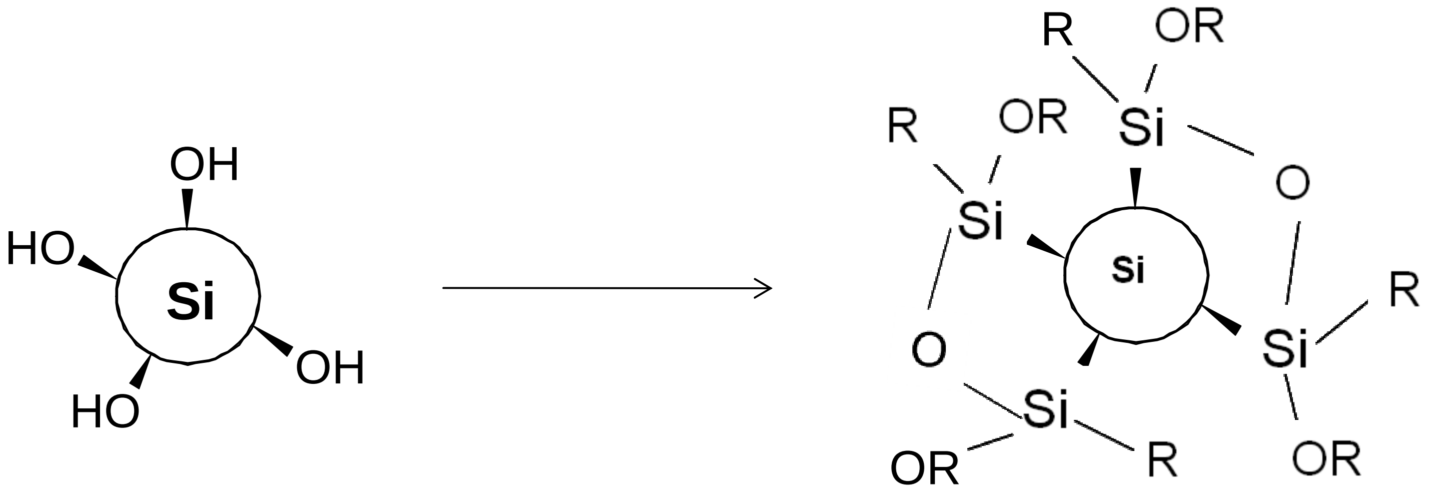
Multi-functional hybrid coating for scratch and corrosion resistance

- silica nanoparticles
(increase scratch resistance, abrasion resistance, flexibility)
- anticorrosive acrylate resin

PHOTOPOLYMERIZATION
Development of photocurable monomer

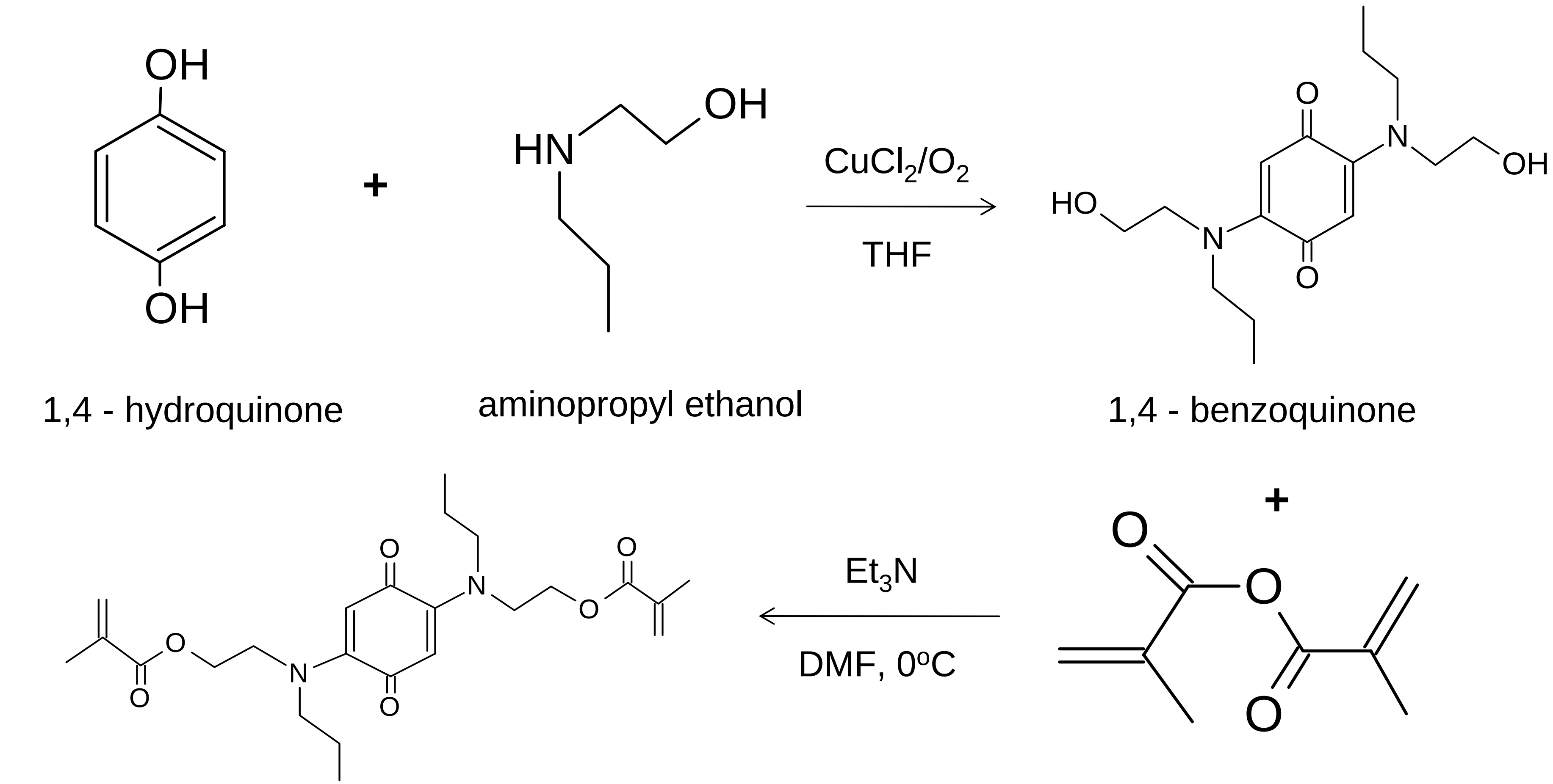
Inorganic nanoparticles (very hydrophilic)	Cannot be dispersed →	Acrylate resins (low polar)

First step: functionalization of nanosilica surface with **alkoxysilanes**



Nanosilica applications for corrosion problems

Second step: Synthesis of anticorrosive di-acrylate (anticorrosive)

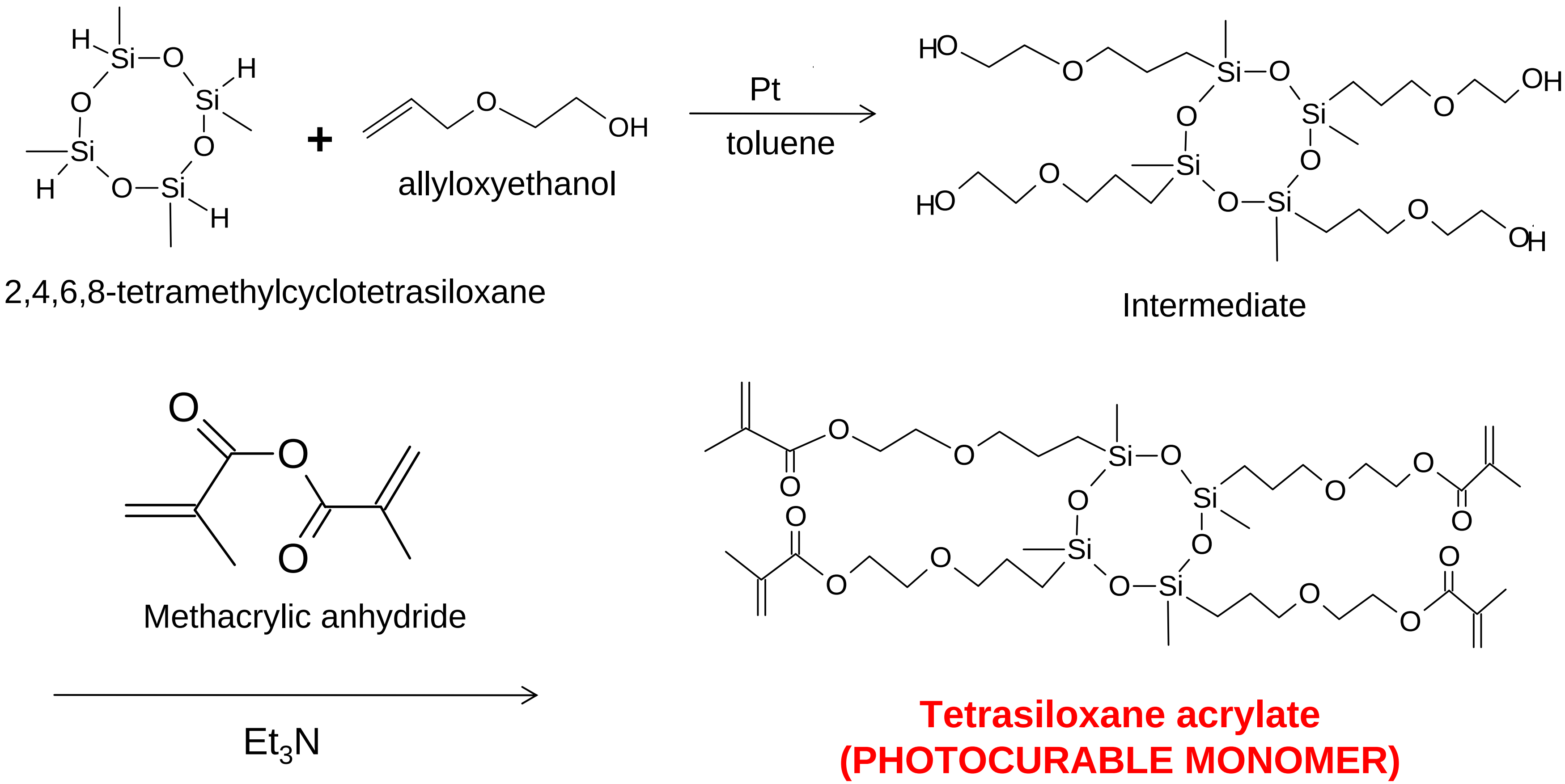


di-acrylate (**anticorrosive speciment**)

methacrylic anhydride

Nanosilica applications for corrosion problems

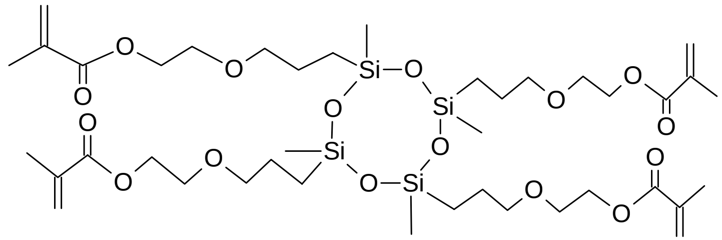
Third step: Syntheses of photocurable monomers



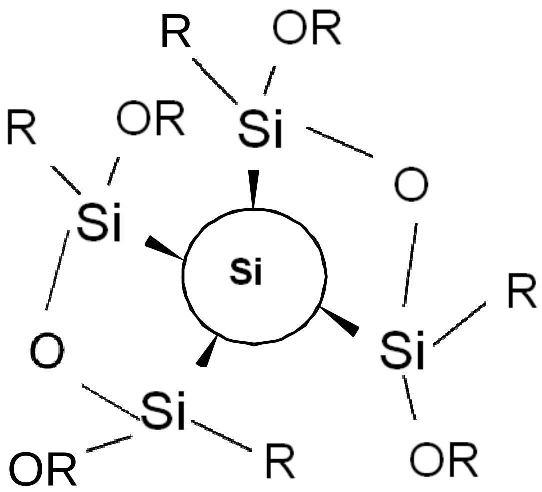
Nanosilica applications for corrosion problems

Third step: Preparation of hybrid coatings

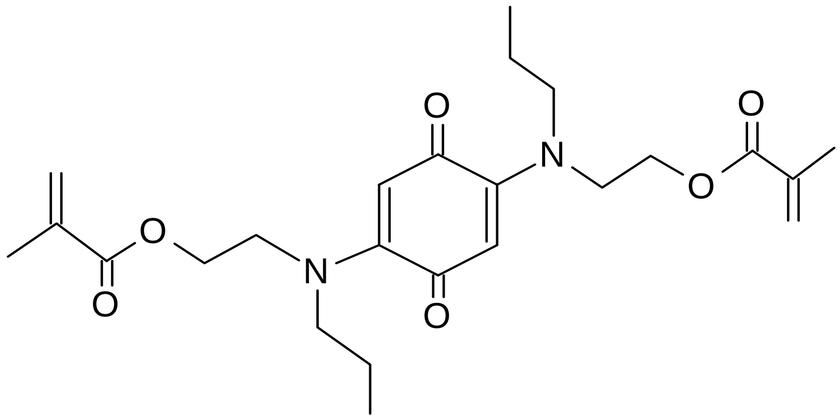
- Functionalized silica nanoparticles
- Anticorrosive di-acrylate



Photocurable monomers



Functionalized silica nanoparticles



Di-acrylate

The coating formulations were **dip-coated** on iron substrates and **photopolymerized by UV irradiation** for 5 min (thicknesses from 10 μm – 12 μm).

RESULTS - Composition of the formulations

	Coating 1	Coating 2	Coating 3	Coating 4
Urethane acrylate	100	---	---	---
Monoacrylate	---	100	---	---
Tetrasiloxane acrylate	---	---	100	100
Anticorrosive acrylate	---	---	---	3

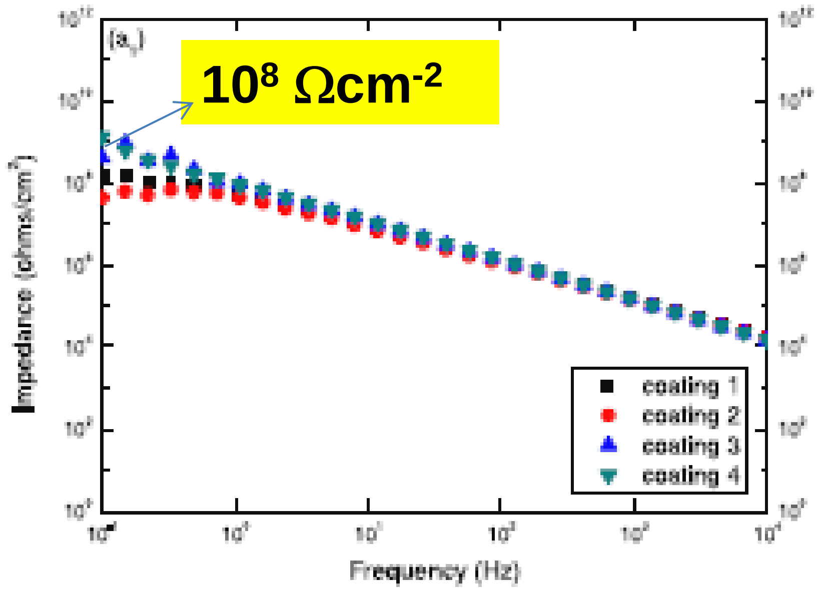
Corrosion studies by Electrochemical Impedance Spectroscopy (EIS)

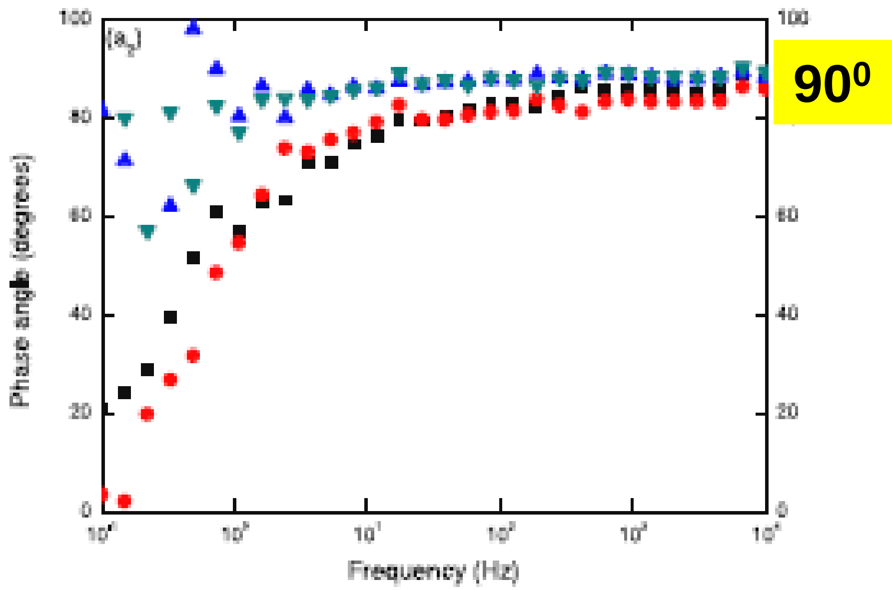
To evaluate the corrosion protection performance of the prepared coatings

Nanosilica applications for corrosion problems

	Coating 1	Coating 2	Coating 3	Coating 4
Urethane acrylate	100	---	---	---
Monoacrylate	---	100	---	---
Tetrasiloxane acrylate	---	---	100	100
Anticorrosive acrylate	---	---	---	3

INITIAL

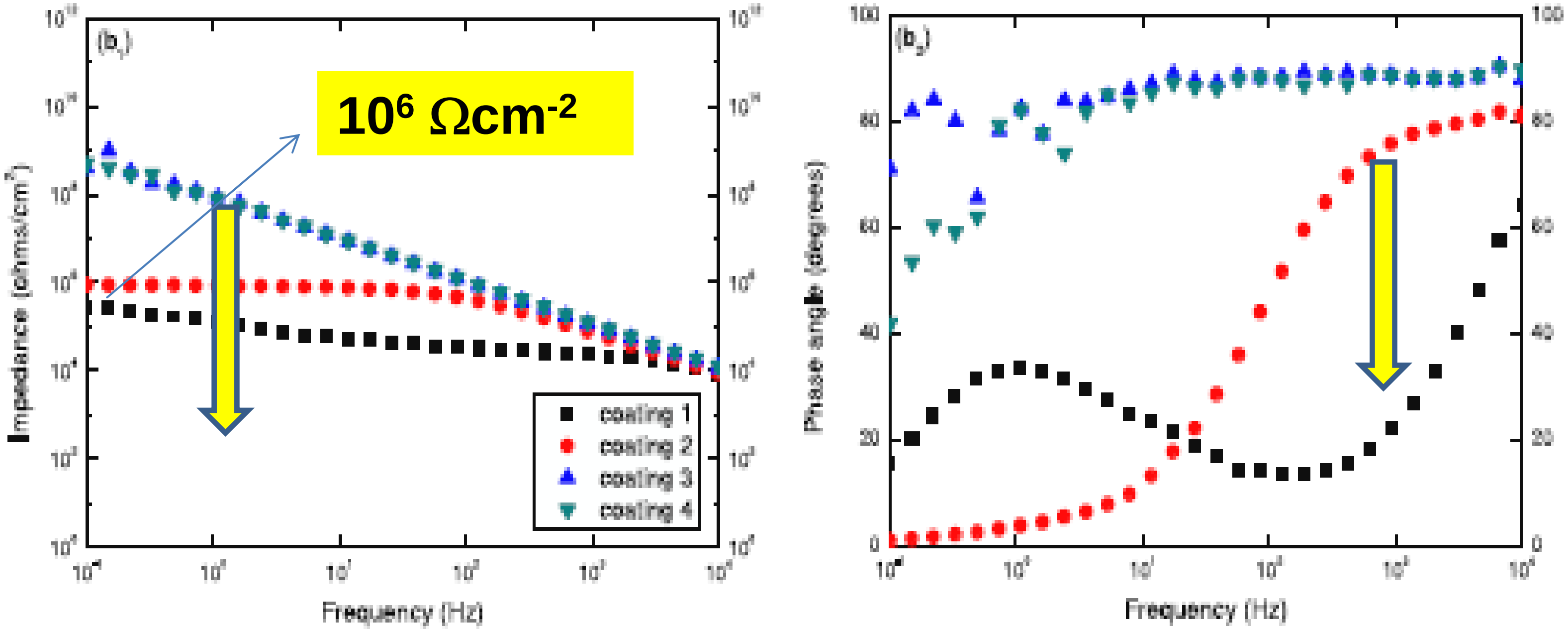




Nanosilica applications for corrosion problems

	Coating 1	Coating 2	Coating 3	Coating 4
Urethane acrylate	100	---	---	---
Monoacrylate	---	100	---	---
Tetrasiloxane acrylate	---	---	100	100
Anticorrosive acrylate	---	---	---	3

AFTER 1 DAY

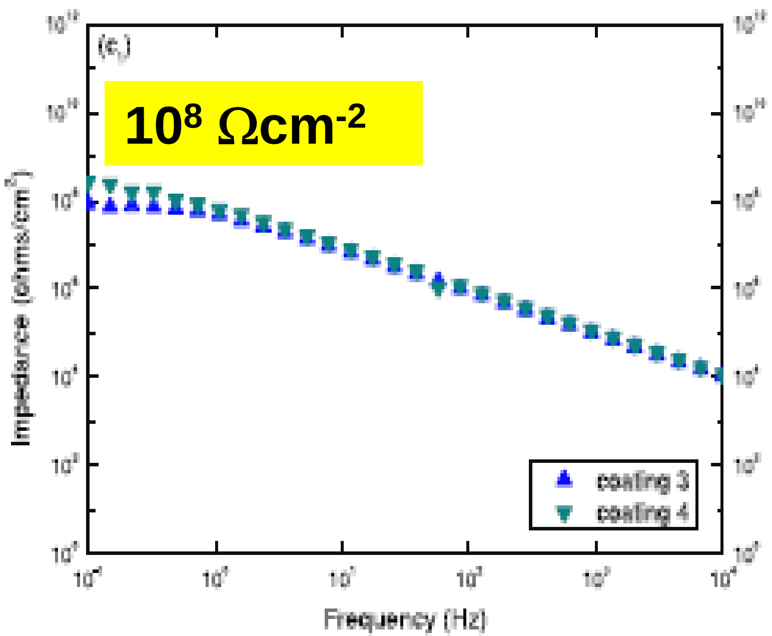


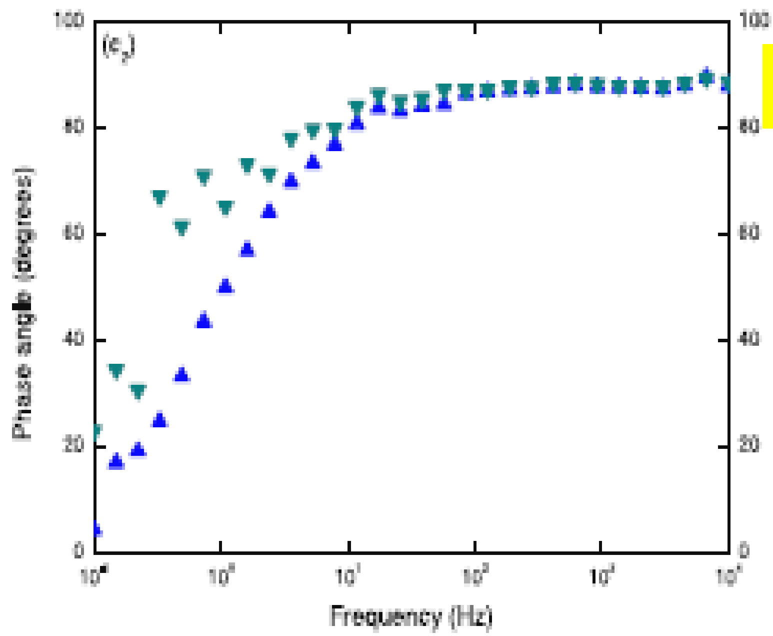
The electrolyte diffused through the coatings 1 and 2

Nanosilica applications for corrosion problems

	1	2	3	4
Urethane acrylate	100	---	---	---
Monoacrylate	---	100	---	---
Tetrasiloxane acrylate	---	---	100	100
Anticorrosive acrylate	---	---	---	3

AFTER 50 DAYS



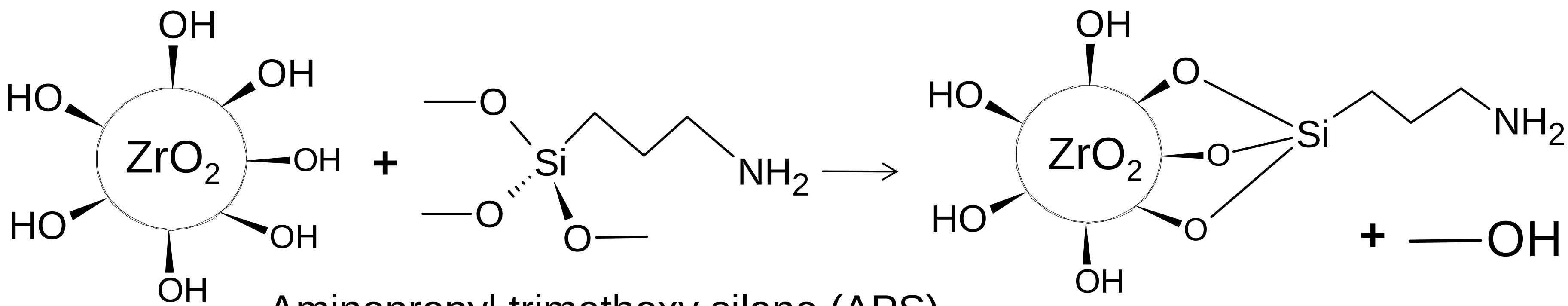


90^0

Corrosion performance of EPOXY COATINGS containing ZrO_2 nanoparticles

- Modification of epoxy coatings by adding various levels of ZrO_2 nanoparticles (1, 2 and 3 wt%)
- To promote chemical interactions between nanoparticles and polymeric coatings, the surface of the nanoparticles

Chemical functionalization

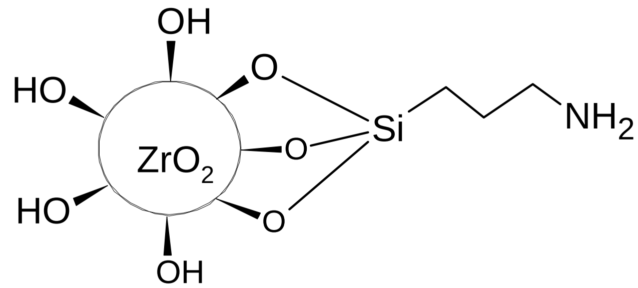


Aminopropyl trimethoxy silane (APS)

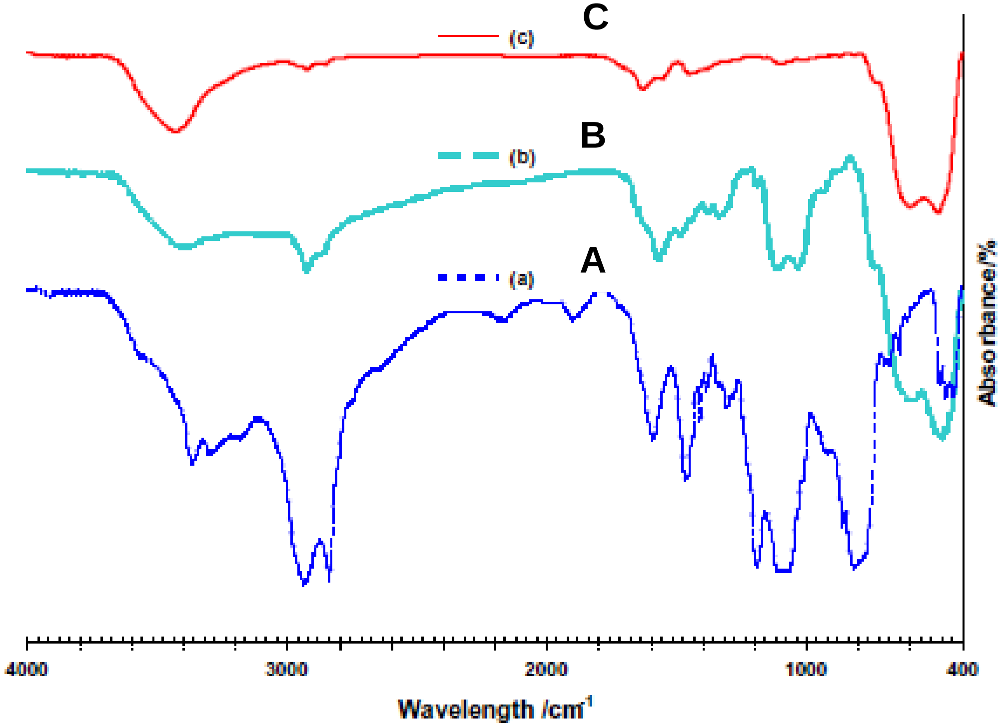
ZrO_2 nanoparticles

ZrO_2 functionalized nanoparticle

Corrosion performance of EPOXY COATINGS containing ZrO_2 nanoparticles



FTIR VIBRATION SURFACE CHARACTERIZATION



A – aminopropyl trimethoxy silane (APS)

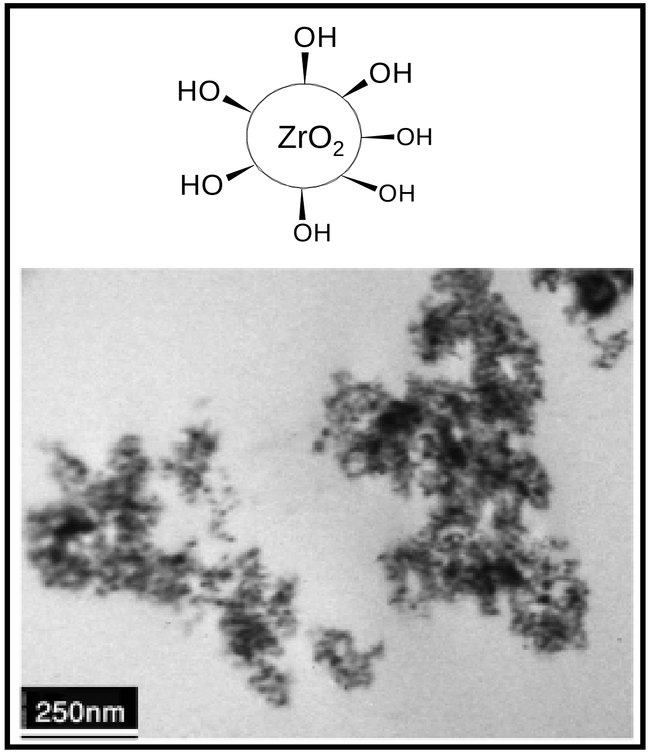
B – untreated ZrO_2 nanoparticles

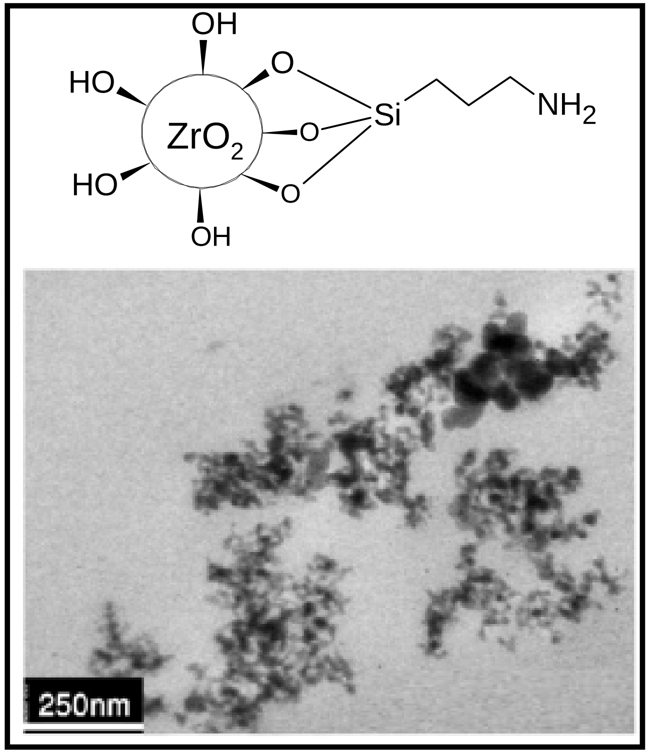
C – APS – treated ZrO_2 nanoparticles

Wavenumber (cm^{-1})	Functionality
490	Stretch vibration band of Si - O
510	Stretch vibration band of Zr – O - Zr
964	Stretch vibration band of Zr – O - Si
1000 - 1300	O – Si asymmetric vibration
1570	Si – O bonds
2870	Symmetric Stretch vibration of $[-(CH_2)_n-]$ and $-(CH_3)$
2930	Asymmetric Stretch vibration of $[-(CH_2)_n-]$ and $-(CH_3$
3430	Vibration band of -OH

Corrosion performance of EPOXY COATINGS containing ZrO_2 nanoparticles

TRANSMISSION ELECTRON MICROSCOPY RESULTS





<u>Aggegation size</u>

- **Relatively dispersed at the scale of 100 – 170 nm**

•Some aggregates particles can be observed (-OH: hydrogen bonding)

Corrosion performance of EPOXY COATINGS containing ZrO_2 nanoparticles

SALT SPRAY TEST RESULTS (2000 hours)

Without nanoparticles

1 wt% ZrO_2

2 wt% ZrO_2
(corrosion was not evident even after 2000 h)

3 wt% ZrO_2
(corrosion was not evident even after 2000 h)

Characterizations techniques

- **NMR** (Nuclear Magnetic Resonance) spectroscopy ^{1}H and ^{13}C;
- **FTIR** (Fourier Transform Infrared in the transmission mode at 400 – 4000 cm^{-1} – degree of modification of the nanoparticles;
- **RAMAN SPECTROSCOPY**
- **TEM** (Transmission Electron Microscopy) images – effect of modification of nanoparticles on their dispersion properties;
- **EIS** (Electrochemical Impedance Spectroscopy) – estimate the corrosion protection performance of the prepared coatings

Conclusions

- Functionalized nanoparticles have been used in anticorrosive coatings
- Development of multi-functional hybrid coating for scratch and corrosion resistance: inorganic (nanoparticle) and organic component (active site)
- Functionalized nanoparticles can be applied in different areas: engineering, medical, biological, etc.

  Its necessary optimize the active sites on the nanoparticle surface (hydrophilic, hydrophobic, conductive etc)
- Characterization technique of nanoparticles surface: NMR, FTIR, Raman, TEM;
- Coating characterization: EIS, salt spray

Thank you !!!