Structure of silver-containing sol-gel hybrid materials and its performance as biocide coatings

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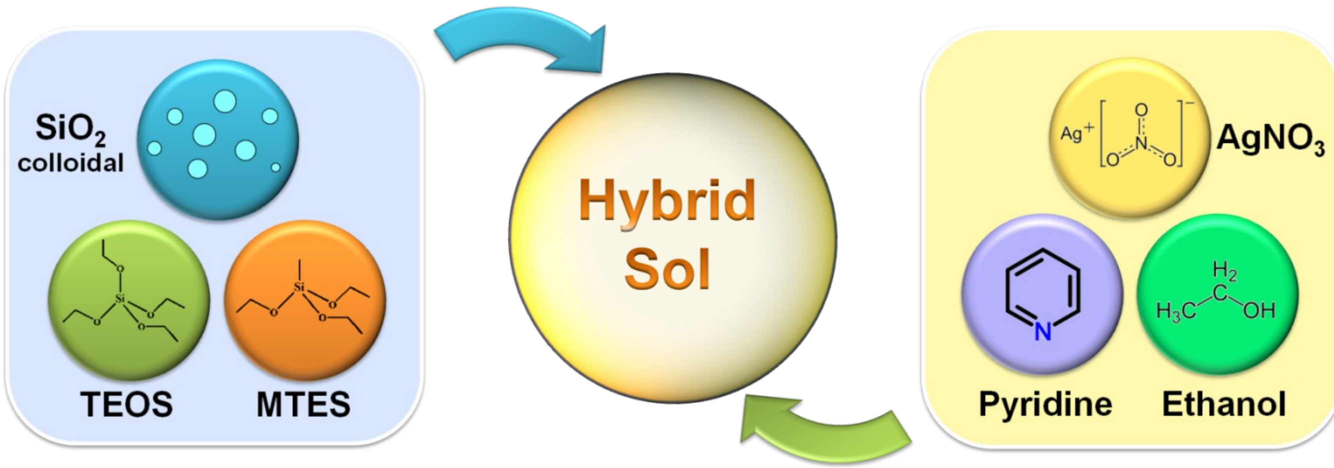
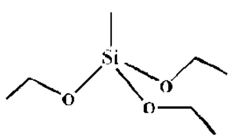
Objectives

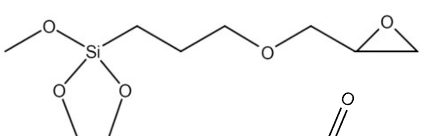
- Development of thin biocide coatings to functionalize surfaces exposed to biologic contamination.
    - To obtain stable hybrid sols able to incorporate Ag^+ ions and inorganic nanoparticles.
    - Deposit a thin and homogeneous coating minimizing Ag^+ loosening by its reduction and agglomeration.
    - To quantify silver releasing (mobility) through hybrid organic-inorganic matrix.
    - To verify the biocide effect by microbiologic

Synthesis of Sols

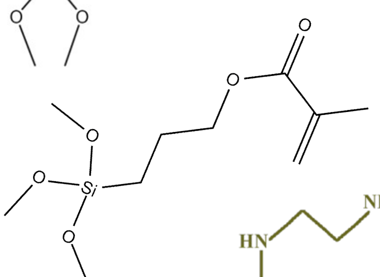




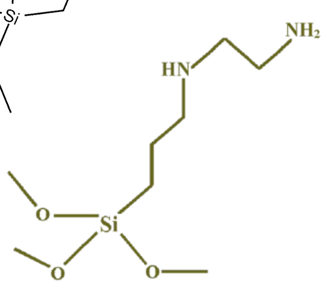
MTES
Methyl-triethoxysilane.



GPTMS
Glycidoxypropyl-trimethoxysilane.



MPS
Methacryloxypropyl-trimethoxysilane.



AEAPTMS
Aminoethylaminopropil-trimethoxysilane.

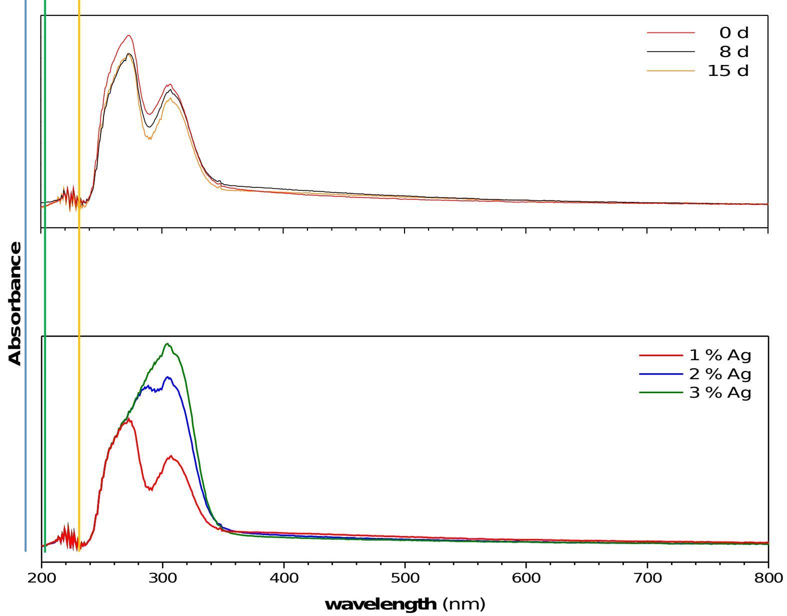
Hybrid Precursors
They give the organic character to the structures, decreasing brittleness and adding chemical functionalities to the network.

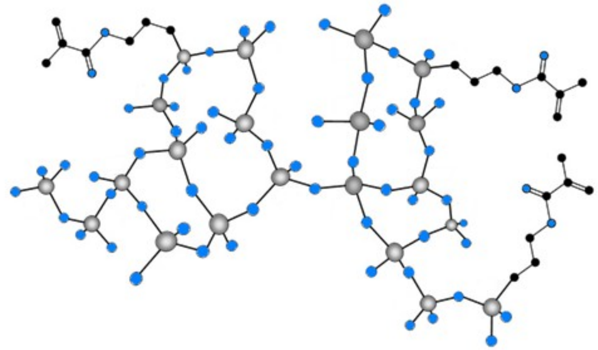
Stability of Sols

Ag8 or higher clusters, at 285 nm.

Ag42+ clusters, at 272 nm.

Ag2+ clusters, at 305 nm.



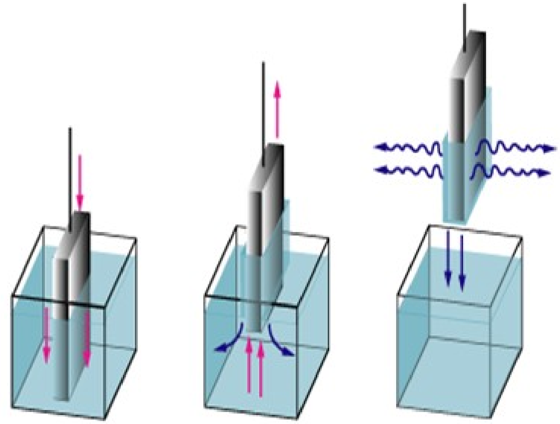


Organic component remains non-reactive under storage conditions.

Inorganic component
O-H and O-R groups are quite stable while solvent is present.

Silver ions
The absence of plasmonic band allows us to assume a certain stability of

Coatings



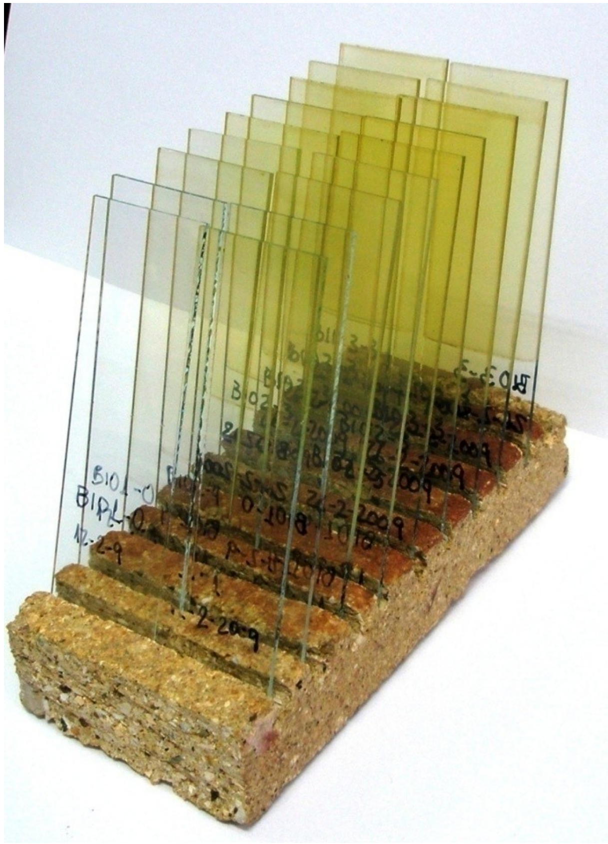
Deposition
Dip-coating process at constant withdrawal rate 10 - 50 cm/min

Drying
At room temperature

Densification
Thermal treatment up to 450 oC, 30 min

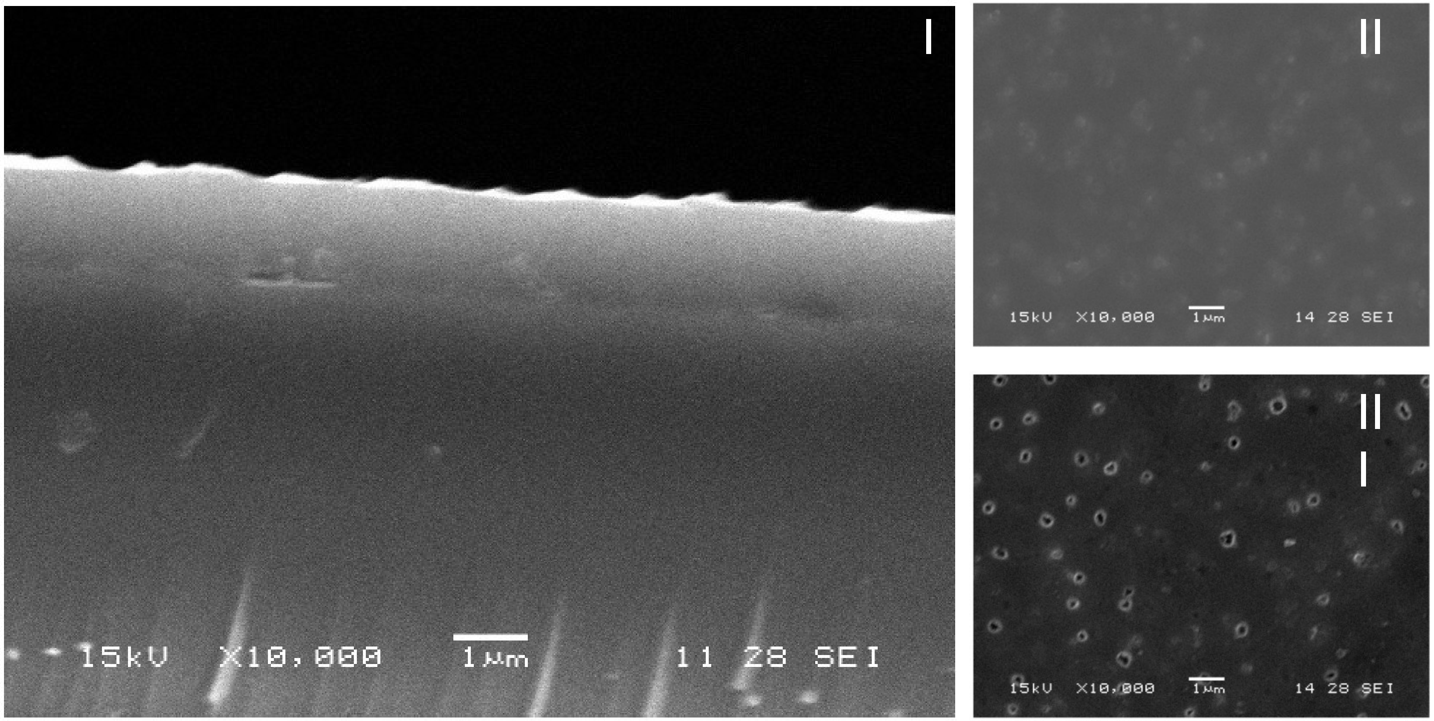
Transparent homogeneous and crack-free coatings were obtained.

A slight yellowish coloration is observed as temperature of thermal treatment or silver concentration increases.



Coatings

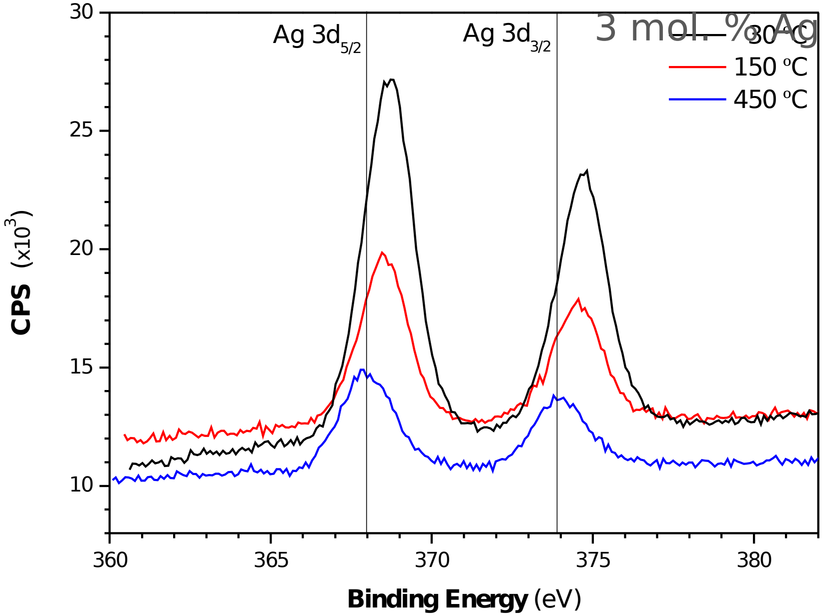
TEOS/MTES/SiO2
3 mol. % Ag
450 oC



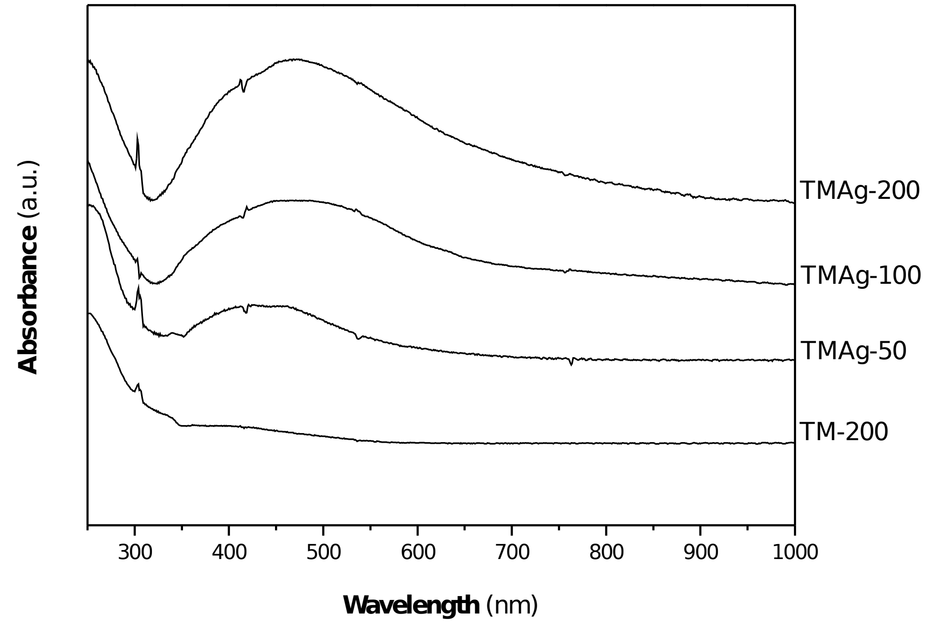
(I) Transversal section: 1.4 µm thick.
(II) Surface: Agglomerates of silver clusters and NP.
(III) Surface (after lixiviation): clearing out of Ag-rich regions.

Silver aggregation

TEOS/MTES/SiO2
3 mol. % Ag



TEOS/MTES
3 mol. % Ag



X-ray photoelectron spectroscopy
Al Kα radiation (1486.7 eV)

The chemical shift from the Binding Energy of metallic silver is higher for samples treated at lower temperatures. At 450 ºC, it reaches the core level value for metallic silver (368.2 eV).

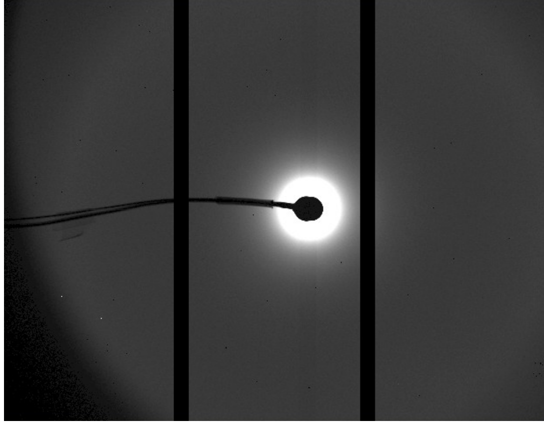
UV-visible spectroscopy

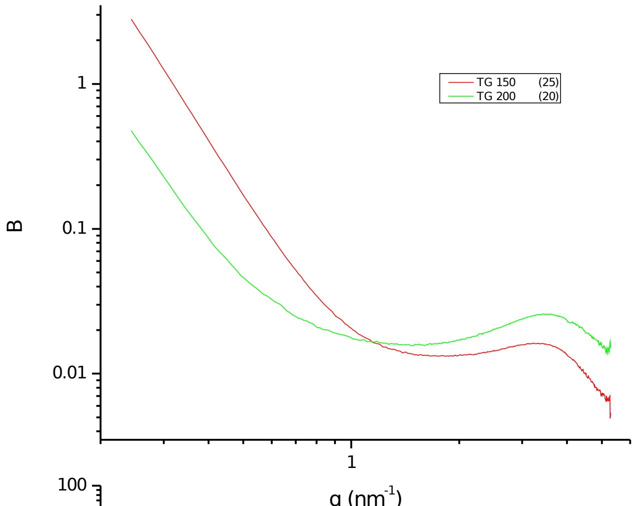
The plasmonic band increases and shifts to higher wavenumbers

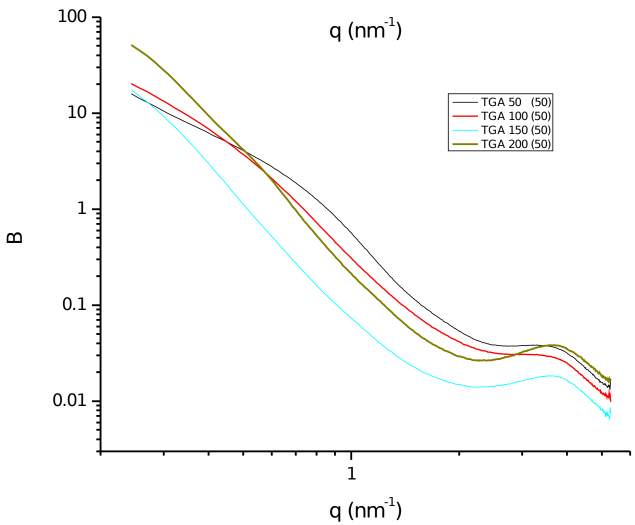
Silver aggregation

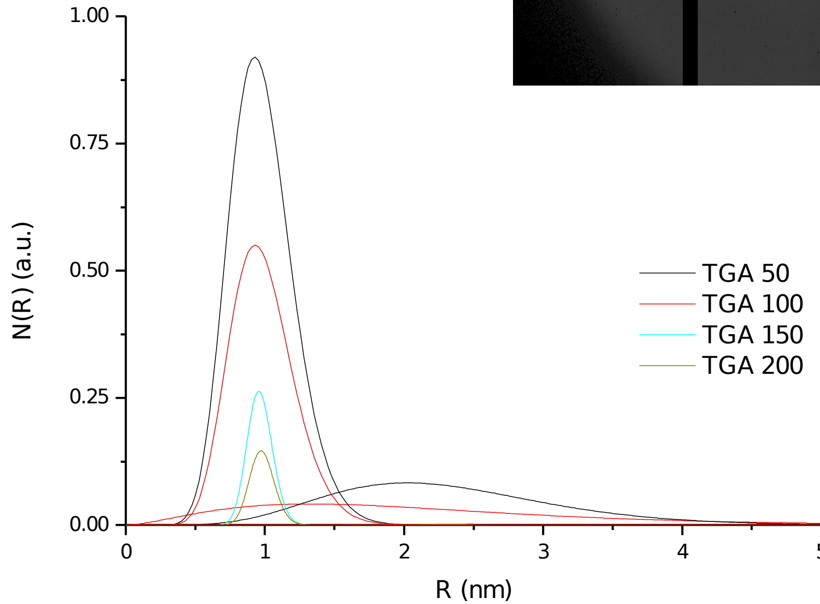
Small angle x-ray scattering
Beamline SAXS1 (LNLS, Brazil)
Synchrotron Light National Laboratory

TEOS/GPTMS
3 mol. % Ag
50 to 200 oC
30 min in air









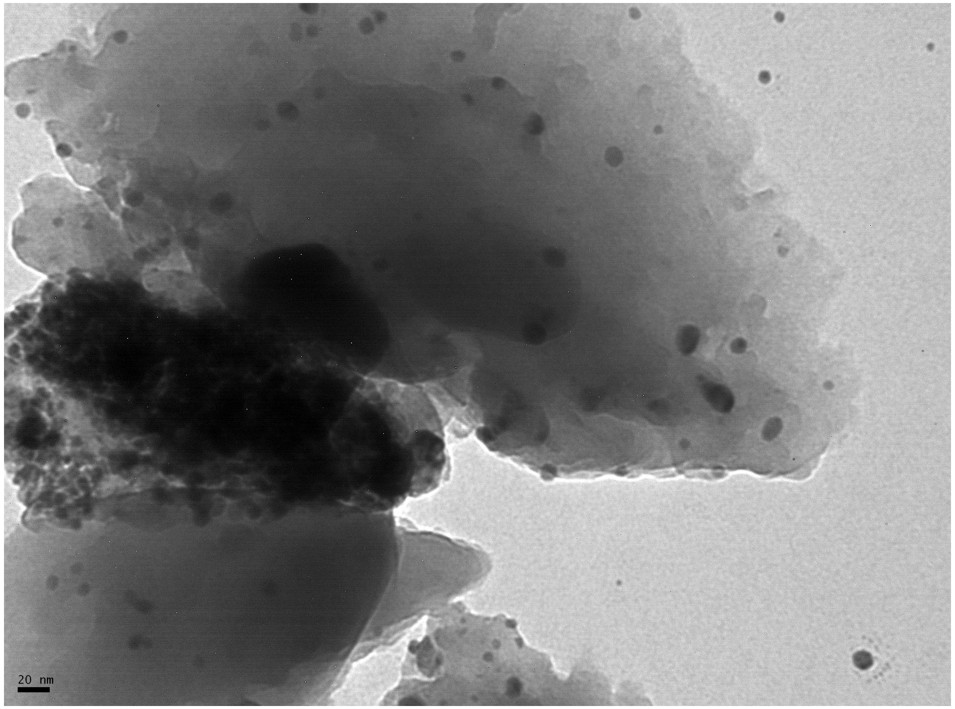
Spherical silver nanoparticles present isotropic distribution.

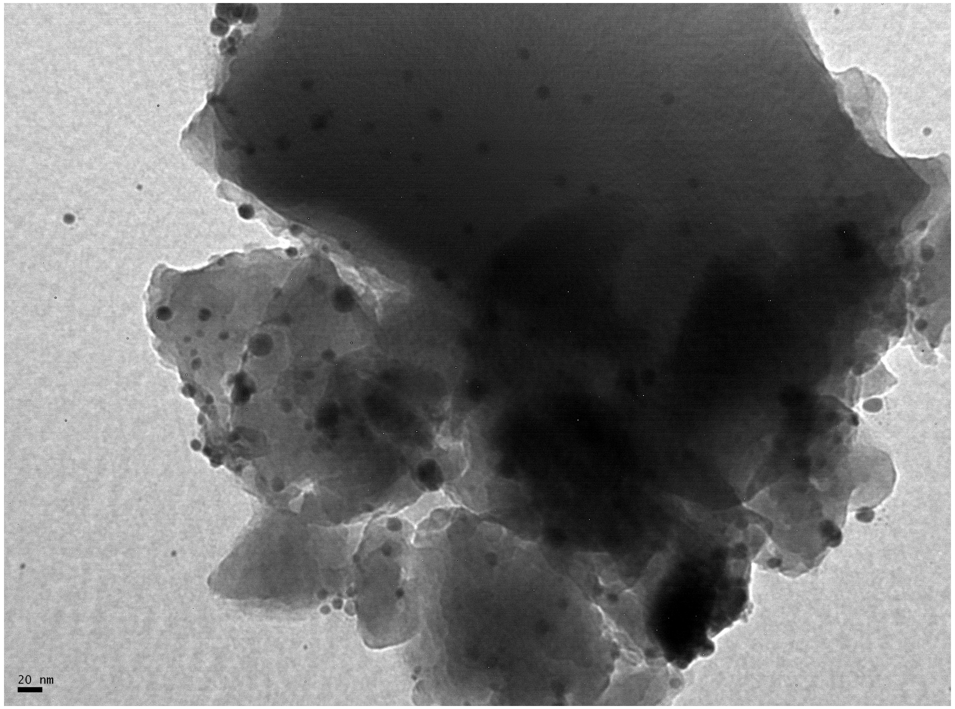
Two main modes were observed around 2 and 4 nm diameter.

As densifying temperature increases, such small particles vanish producing higher silver nanoparticles.

Silver aggregation

TEOS/GPTMS
3 mol. % Ag
150 oC, 30 min in air



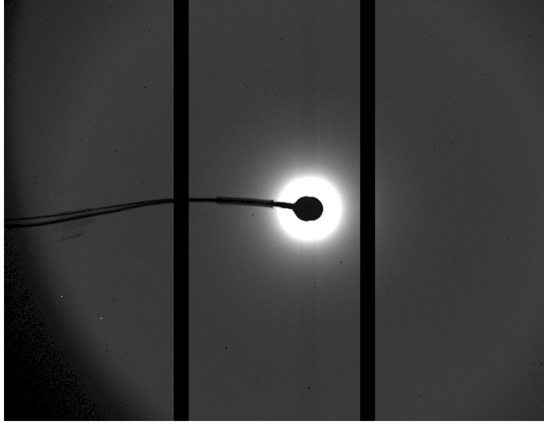


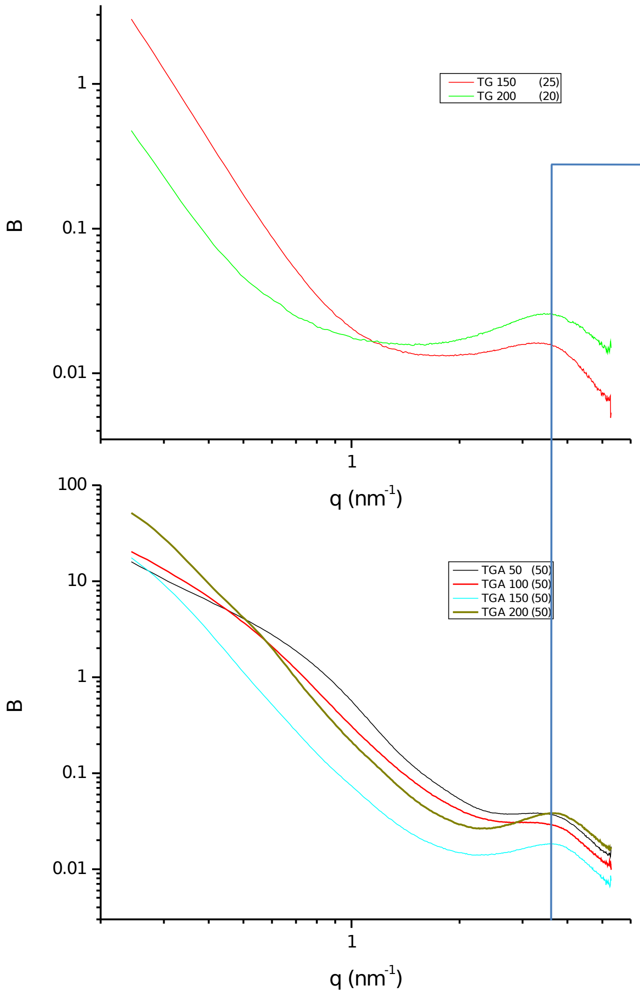
Silver nanoparticles of up to 20 nm diameter.

Matrix structure

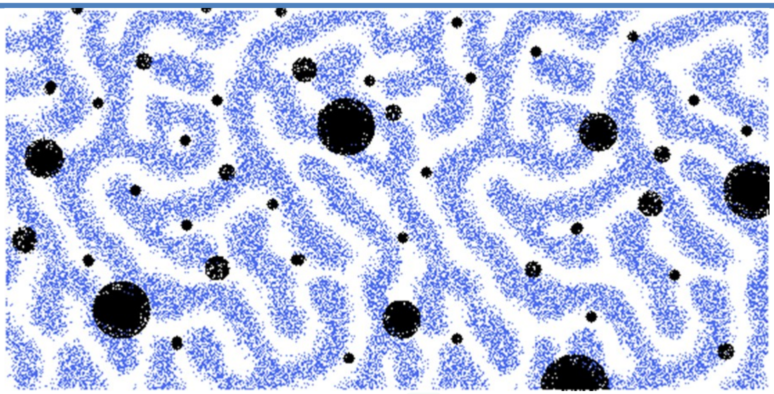
Small angle x-ray scattering
Beamline SAXS1 (LNLS, Brazil)
Synchrotron Light National Laboratory

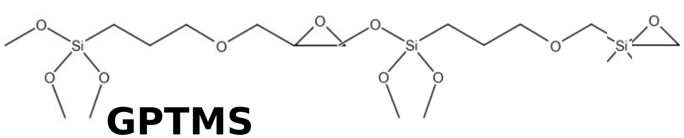
TEOS/GPTMS
3 mol. % Ag
50 to 200 oC
30 min in air





Bi-continuous and non-particular structure. *Teubner-Strey.*
Independent of thermal treatment and silver doping.





GPTMS

GPTMS

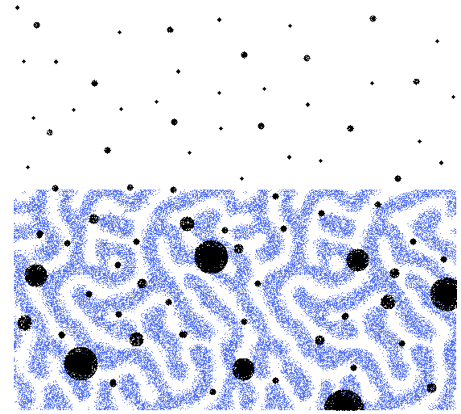
Silver release

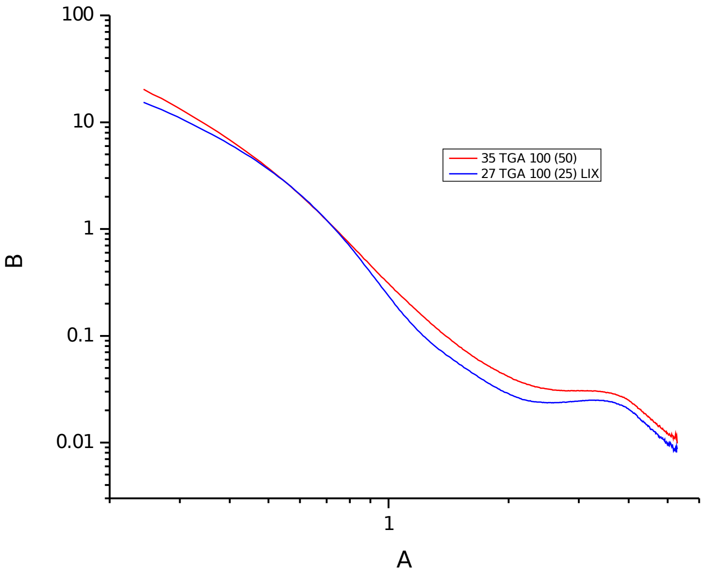
in water at 30 oC

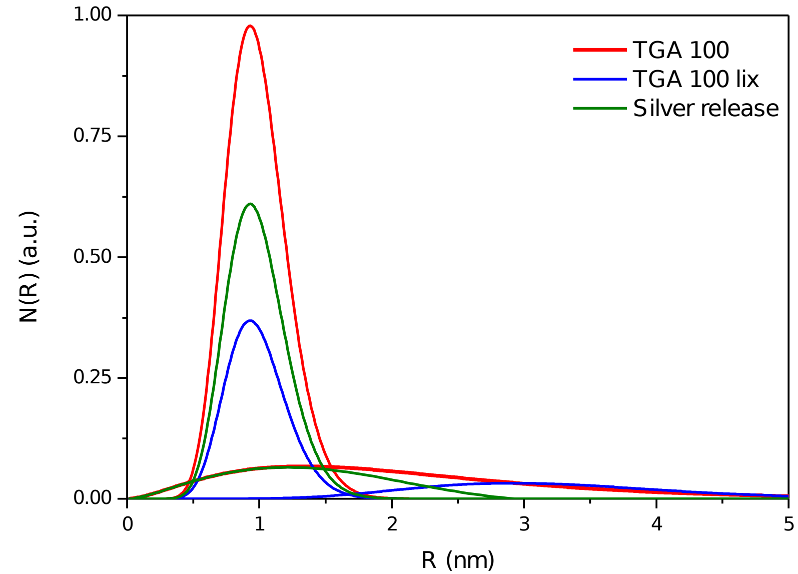
TEOS/GPTMS

3 mol. % Ag

100 oC, 30 min in air





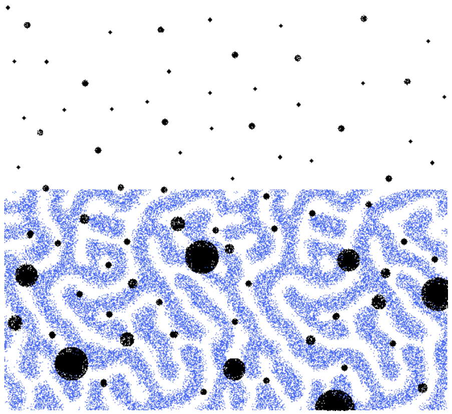


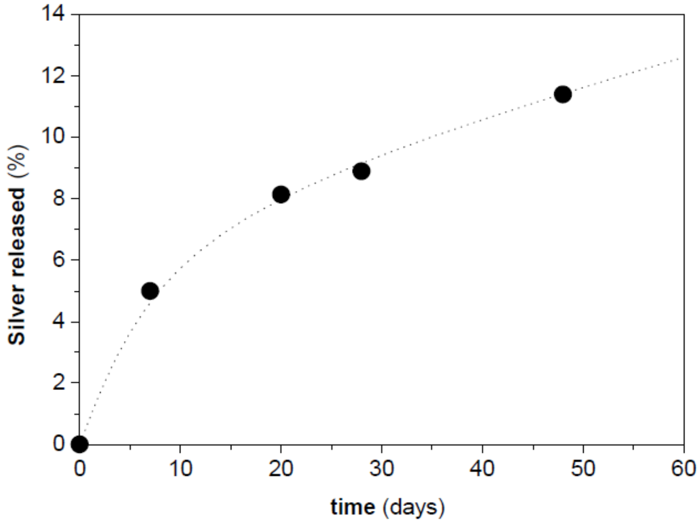
The difference, in SAXS spectra, between lixiviated and non-lixiviated samples reveals that particles over 4 nm of size are mainly not released from the hybrid structure.

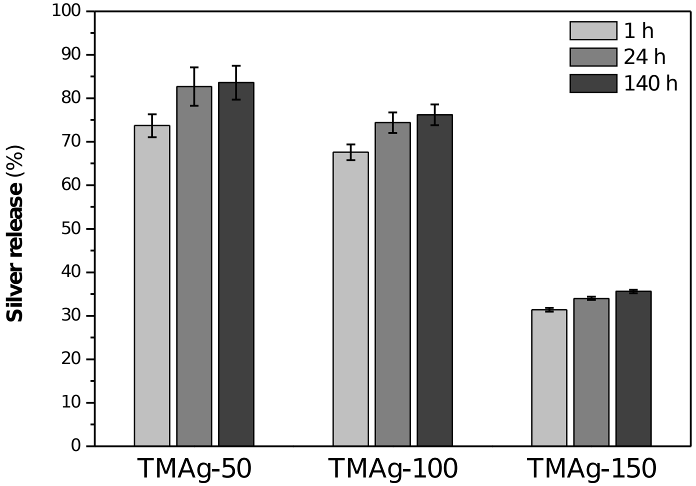
Silver release

in water at 30 oC

TEOS/MTES/SiO2
3 mol. % Ag
450 oC







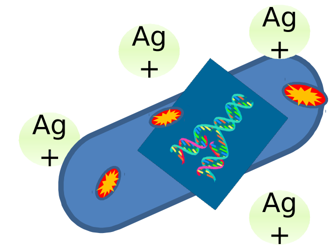
TEOS/MTES
3 mol. % Ag
50 – 150 oC

Both silver release rate and silver availability to be released are governed by structural factors related to the coating matrix, as crosslinking of the network and density.

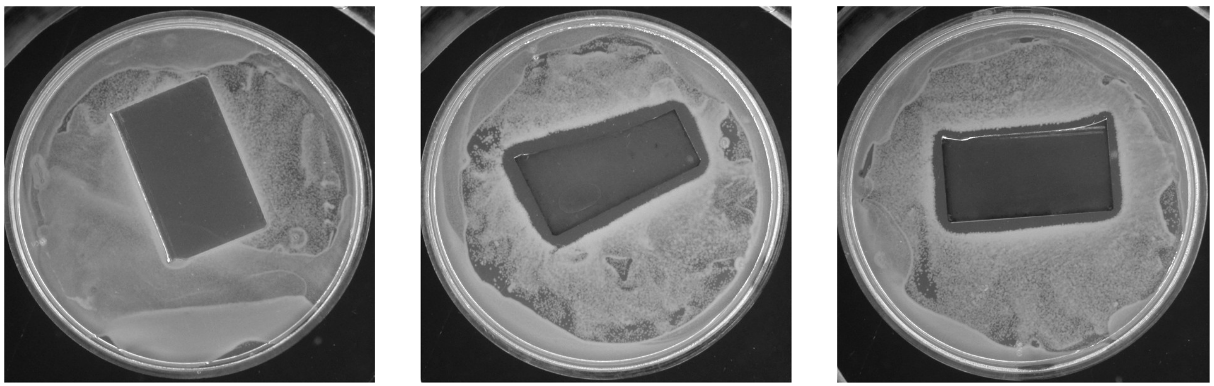
Thermal treatment silver nanoparticles growing → loosening of efficiency
crosslinking and density → structural integrity

Incorporation of silica nanoparticles allowed to achieve a gradual silver liberation up to near two months of immersion.

Biocide effect

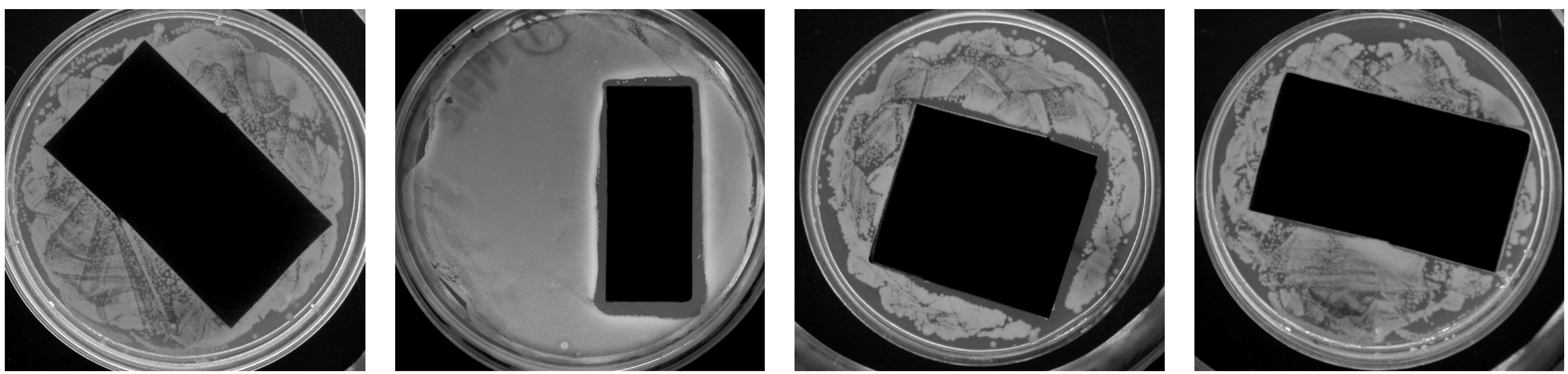


On Glass substrate



Inhibitory halos in agar diffusion tests of Escherichia coli cultures for 3 mol % Ag doped coatings.

On Stainless Steel



control | 50 °C | 150 °C | 450 °C

The size of the inhibitory halos keep tight relation with the temperature of the densifying treatment, *i.e.*, with the availability and mobility of silver ions and smaller nanoparticles.

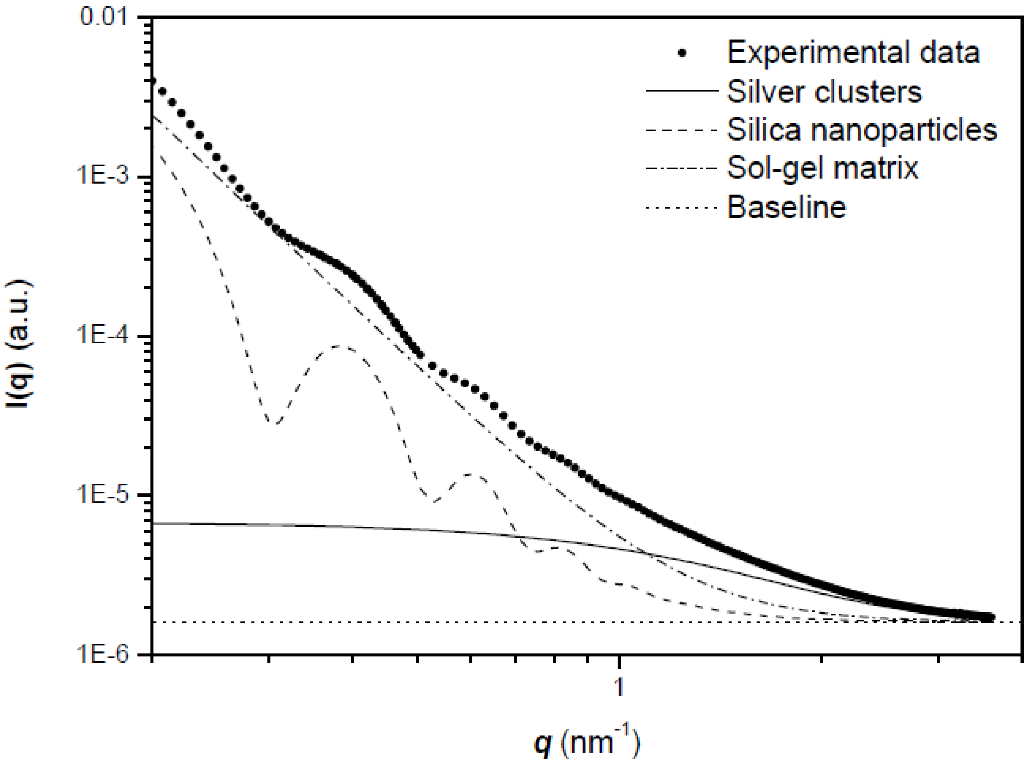
Conclusions

- Stable hybrid sols were obtained minimizing the reduction of silver ions, even in highly organic sols.
- Silver stabilization weakens as thermal treatment becomes more intense leading to loosing of the biocide efficiency.
- Incorporation of dense nanoparticles, as silica nanoparticles or nano-clays, appears as a promising alternative to achieve a long-term effective biocide hybrid coating.

THANKS

TEOS/MTES/SiO2

3 mol. % Ag



SAXS FITTING

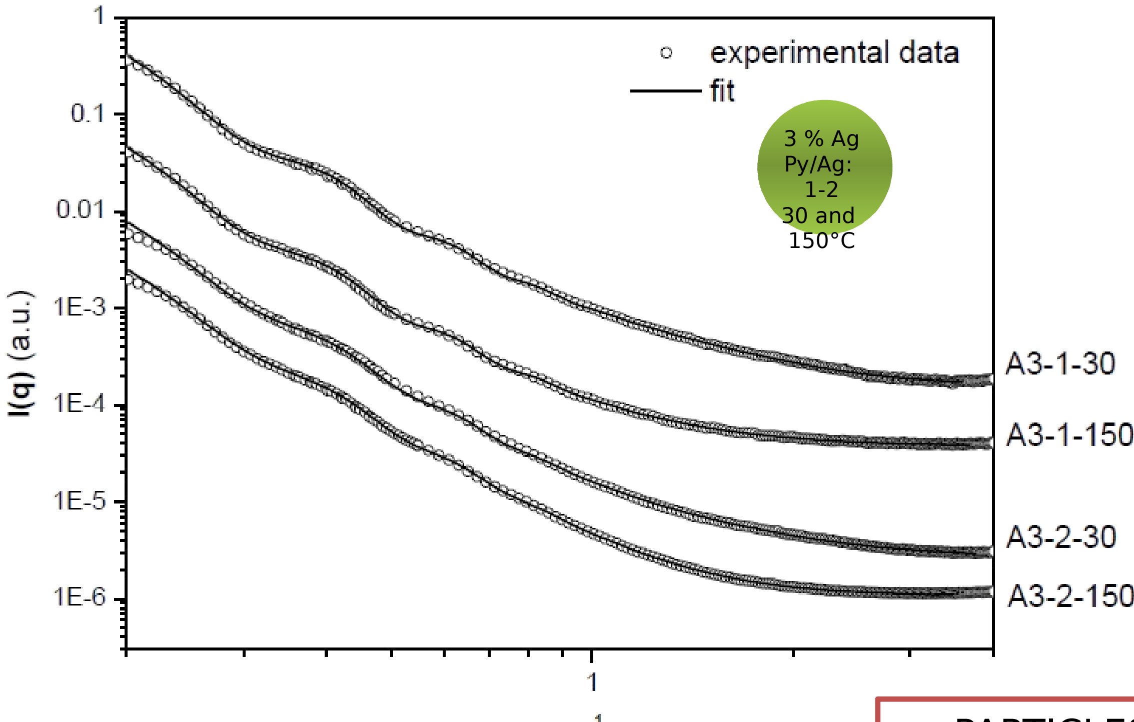
SAXS data were processed by the SASfit software package.

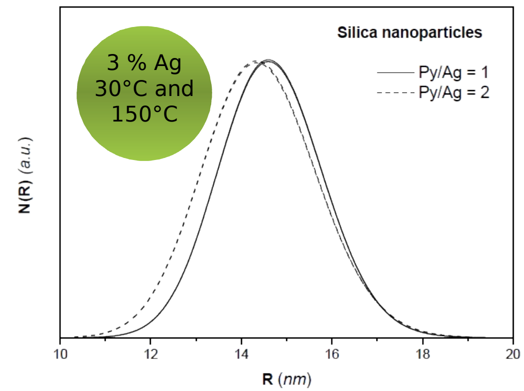
SAXS results were fitted according to a bimodal Schultz–Zimm distribution (SZ) of spherical solid silver and silica nanoparticles. The Schultz–Zimm distribution derives from thermodynamic theories and is of particular importance to describe particles distributions, having a better match to reality than the normal Gaussian distribution.

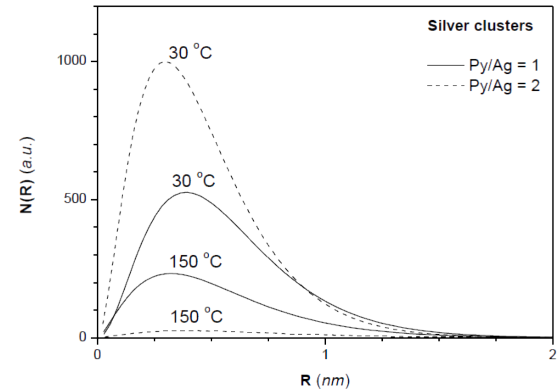
- Hybrid structures and thermal evolution of silver nanoparticles were analyzed by Small Angle X-ray Scattering (SAXS) through synchrotron radiation. A spinodal-like phase separation was resolved in each one of the hybrid matrixes. Although the biocide effect was verified against Escherichia coli, through the inhibition halo in agar diffusion tests, diffusion analysis suggest that a matrix modification, with incorporation of denser ceramic nanoparticles, could increase use life of biocide coatings.

TEOS/MTES/SiO2

3 mol. % Ag







THERMAL EVOLUTION OF Ag DOPED COATINGS

- During synthesis of sols, the progress of hydrolysis and condensation carry to agglomeration of silica NP, superficially enriched with Si-OH groups, from 3 to 14.5 nm of radius.

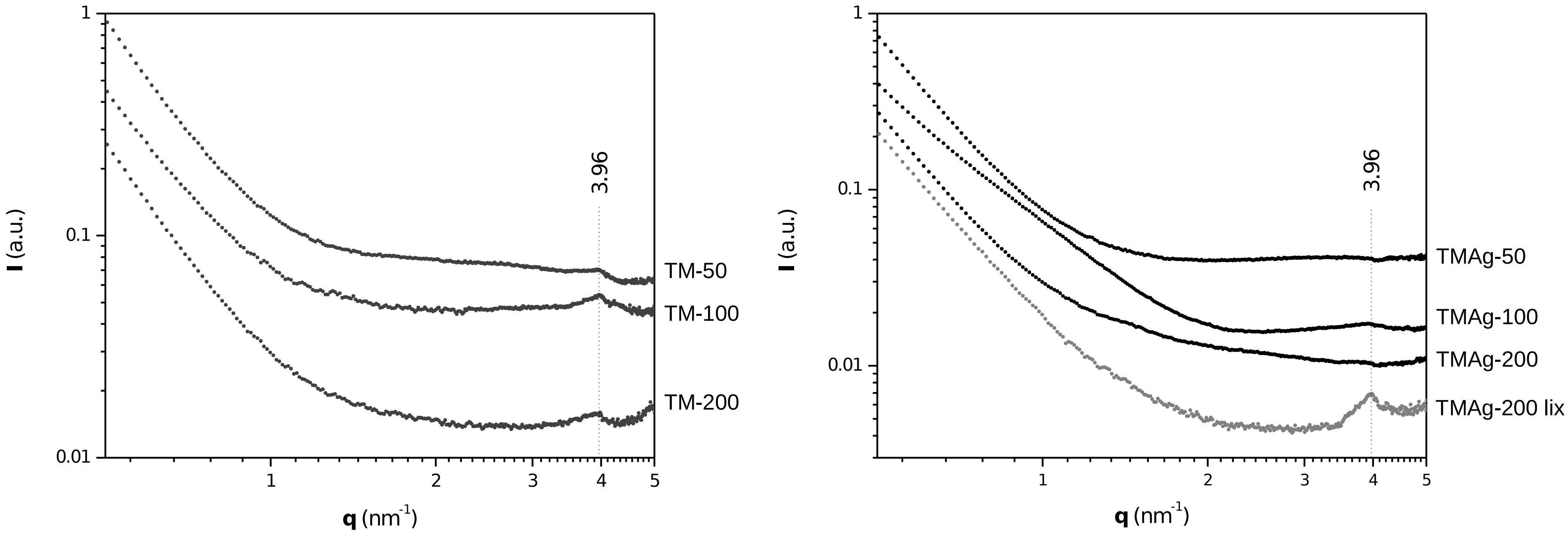
PARTICLES SIZE DISTRIBUTION

Silver clusters:

A strong change occurs during thermal treatment.

SAXS fitting reveals evolution of subnanometrical silver particles in a monomodal size distribution (around 0.3 nm of radius), in agreement with Ag8 clusters and its isomeric ions detected by UV-Visible spectroscopy.

TEOS/MTES
3 mol. % Ag



SAXS curves obtained for *a*) TM and *b*) TMAg coatings as a function of thermal treatment and TMAg coating treated at 200 ºC and lixiviated for 140 h in deionized water.

The position of the peak, at 3.96 nm-1, is associated to a characteristic length given by 2π/qmax = 1.6 nm