

Development of Silver Clusters in Hybrid Organic-Inorganic Sol-Gel Coatings

Procaccini, R.A.,¹ Cere, S.¹ and Pellice, S. A.¹

¹Instituto de investigación en ciencia y tecnología de materi - Mar del Plata BA Argentina

INTRODUCTION

A silver doped hybrid organic-inorganic sol-gel coating was developed through the hydrolytic condensation of tetraethoxysilane (TEOS) and methyl-triethoxysilane (MTES). Silica nanoparticles were added in order to give a mechanical reinforcement and silver nitrate as the supplier of Ag^+ ions, which have a potential effect as a biocide component. A high thermal sensitivity of sub-nanometric silver particles was determined by Small Angle X-ray Scattering (SAXS) carrying to formation of higher agglomerates or silver nanoparticles.

EXPERIMENT

Hybrid sols were prepared by the chemical reaction, in acidic conditions, of tetraethoxysilane (TEOS) and methyl-triethoxysilane (MTES) in presence of an aqueous dispersion, 40 vol.%, of colloidal silica (LUDOX AS-40 Aldrich, $d = 6$ nm). TEOS/MTES/ SiO_2 (NP) molar ratio was kept at 36/54/10. Silver doping was performed through the addition of a pyridine stabilized solution of AgNO_3 and absolute ethanol. Pyridine/Ag molar ratios of 2/1 and 1/1 were analyzed in this work. Through the dip-coating process, at 25 cm/min of withdrawal speed, homogeneous coatings with 1, 2 and 3 mol % of Ag were obtained and were exposed to densification at 30, 150, 300 and 450 °C, in air atmosphere during 30 minutes. Development of silver nanoparticles in coatings, as a function of pyridine/silver ratio and thermal treatment, was analyzed through SAXS using the beam lines SAXS1 and SAXS2 of the National Laboratory of Synchrotron Light. Coatings were taken out from glass substrates by scratching producing glassy powders which were placed in the sample holders by adhesive polyimide film (Kapton ®, DuPont). To cover a wide range in the q -space, two geometrical configurations were set up, a sample detector distance of 80 mm with monochromatic light of $\lambda = 1.608$ Å (SAXS1) and a sample detector distance of 614 mm with monochromatic light of $\lambda = 1.488$ Å (SAXS2). The Q range was calibrated using silver behenate, which have a well-known lamellar structure with $d = 5.848$ nm. SAXS data were processed by the SASfit software package [1] using the theoretical values of the X-ray scattering length densities of silver ($7.744 \times 10^{-3} \text{ nm}^{-2}$), silica ($1.922 \times 10^{-3} \text{ nm}^{-2}$) and the hybrid matrix ($1.140 \times 10^{-3} \text{ nm}^{-2}$) for the fitting procedure. SAXS results were fitted according to a bimodal Schultz-Zimm distribution (SZ) of spherical solid silver and silica nanoparticles.

RESULTS AND DISCUSSION

After dip-coating, drying and thermal treatment, the matrices of obtained films acquire hardness and get a denser structure. On the other hand, silver ions and clusters are susceptible to undergo a process of loosening of pyridine coordination and the consequent destabilization of the arrangement achieved by silver in the sol state, this phenomenon gives place to coalescence and agglomeration processes producing higher silver nanoparticles. [2] Through SAXS experiments, a detailed analysis of particle distribution could be done. Figure 1 shows, as instance, the SAXS spectrum and fitting of a sample obtained from a 3% Ag sol, with Py/Ag ratio of 2, thermally treated at 30 °C. In this case, the experimental setup al-

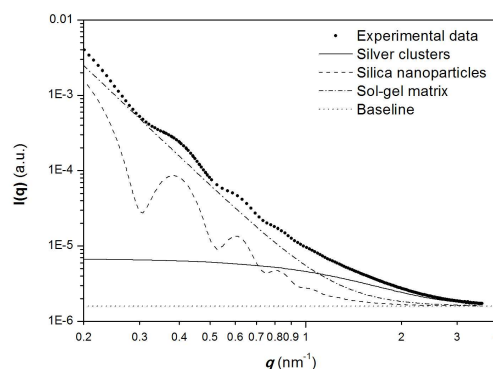


FIG. 1: SAXS spectra of 3 mol% Ag doped coatings. Components of the fitting for a sample thermally treated at 30 °C with a molar ratio Py/Ag=2.

lows a good determination of the baseline from the asymptote at higher q values. Three main components are clearly observed: a) a curve characteristic of a sol-gel matrix, b) a wavy line, attributed to a narrow size distribution of silica nanoparticles and c) a curve corresponding to silver clusters. Due to the double logarithmic scale, it is noticeable that silver clusters has the higher contribution at $q > 1 \text{ nm}^{-1}$ values. Figure 2 shows SAXS curves, and their corresponding fits, of samples doped with 3 mol % Ag, Py/Ag ratios of 1 and 2, and thermally treated at 30 and 150 °C. The process of hydrolytic condensation in presence of silica nanoparticles produces their surface modification (grafting) through covalent bonding to partially hydrolyzed TEOS and MTES. As hydrolysis and condensation progress, nanoparticles superficially enriched with Si-OH groups, undergo agglomeration growing from 3 nm to 14.5 nm of radius approximately. This result is in accordance with a previous work where those silica nanopar-

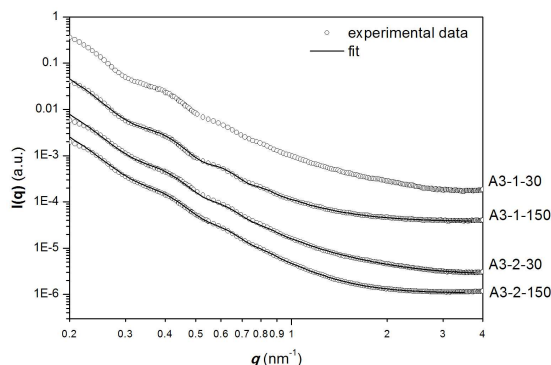


FIG. 2: Experimental data and corresponding fitting curves.

ticles were incorporated to a hybrid silica-methacrylate sol. [3] Although this silica agglomeration implies a hierarchical structure where agglomerates are composed of smaller silica nanoparticles, those constitutive nanoparticles are not revealed by SAXS experiments. Presumably, this effect is a consequence of a tight percolation of those silica nanoparticles during the hydrolytic process. Thus, silica nanoparticles would be embedded into a local matrix of similar light scattering density, which constitutes the observed agglomerates. Taking in account that this agglomeration occurs during the synthesis process, and that those agglomerates are covalently bonded to the hybrid matrix by Si-O-Si bonds, it is clear that no changes are possible in their size distribution as a function of the thermal treatment of coatings, as it was experimentally observed. Temperature has no effect on silica nanoparticles size distributions, curves corresponding to 30 °C and 150 °C are perfectly superimposed; figure not showed. During deposition, drying and thermal treatment of silver doped coatings, a strong change occurs to silver clusters. SAXS fittings reveal the evolution of subnanometrical silver particles in a monomodal size distribution with the mode around of 0.3 nm of radius, Figure 3. Such particle size agrees with the matching for Ag₈ clusters and its isomeric ions (ca. 5 Å diameter) [4]. Two well differentiated behaviors were observed as Py/Ag ratio increases from 1 to 2. Although, at 30 °C, coatings with a ratio Py/Ag=2 has approximately the twice of particles than coatings with ratio Py/Ag=1, its distribution is slightly sharper and, as a result, the volumetric integration reveals that the amount of silver distributed in those clusters differs only by a 9.5 %. Upon thermal treatment in air atmosphere, coordination between silver and pyridine is broken and the reduction of Ag⁺ to Ag⁰ takes place with agglomeration and growing of silver clusters and nanoparticles. Such reduction process is increased by interaction with the surrounding matrix and the organic components. Therefore, when coatings are exposed to a thermal treatment of 150 °C, an expectable diminution in the amount of silver clusters is observed; coatings with ratios Py/Ag=1 and 2 loses respectively 54 and 92 vol.%. That loosening of silver clusters with temperature could impose strong

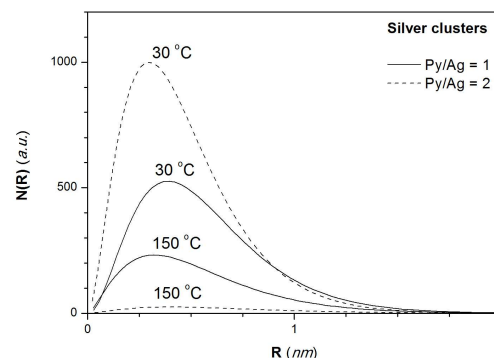


FIG. 3: Size distribution of silver clusters on samples with 3 mol % of Ag thermally treated at 30 and 150 °C.

limitations for production of biocide coatings with these processing conditions. Falletta et al. [5] found bactericidal behavior in fabrics soaked with ultra-small silver particles (0.6 nm of radius) doped sols.

CONCLUSION

Silver doped hybrid organic-inorganic sol-gel coatings were synthesized by hydrolytic condensation of TEOS and MTES in presence of silica nanoparticles. Pyridine coordination of silver ions carried to the development of silver clusters and allowed the stabilization of sols for more than two months of ageing in dark conditions at 4 °C without precipitation or loosening of colourless. Upon thermal treatment, silver clusters undergo agglomeration leading to formation of nanometric and sub-nanometric particles detected by SAXS.

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