

In situ generation of silver microstructures by thermal decomposition of silver *n*-dodecanethiolate dispersed in an organic–inorganic hybrid coating

María L. Gómez, Cristina E. Hoppe, Roberto J.J. Williams*

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina

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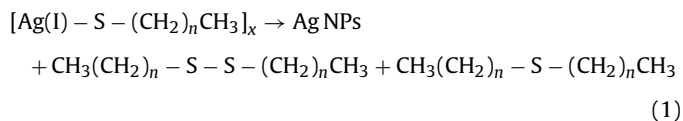
ABSTRACT

Although it is known that metallic silver can be produced by the thermal decomposition of silver *n*-dodecanethiolate (Ag-DDT), the use of this reaction to synthesize silver-modified coatings is difficult due to the insolubility of Ag-DDT in most solvents and coating precursors. We report that lamellar Ag-DDT crystals can be uniformly dispersed in an organic–inorganic hybrid coating based on a bridged silsesquioxane containing pendant dodecyl chains. Heating the dispersion for 4 h at 423 K (above the melting point of the Ag-DDT crystals) produced the transformation of the lamellar phase into a metastable crystalline phase together with a spiral-like microstructuration of the whole material. When the heating was continued for 24 h, the metastable crystalline phase led to metallic silver microstructures uniformly dispersed in the silsesquioxane matrix.

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1. Introduction

Coatings containing a dispersion of silver nanoparticles (Ag NPs) exhibit interesting properties such as antimicrobial activity [1–7], surface-enhanced Raman scattering [8,9], and specific optical and electrical properties [10–13]. A large variety of experimental techniques have been employed to produce the dispersion of Ag NPs, including the employment of preformed nanoparticles or their in situ generation inside the coating. Silver *n*-alkanethiolates can be used as precursors for the generation of Ag NPs by thermal decomposition [14–17]. The reaction may be described by a similar equation as the one proposed for Au(I) *n*-alkanethiolates [18]:



The resulting Ag NPs are stabilized by *n*-alkanethiolate chains bonded to silver atoms present at the surface of NPs.

However, the insolubility of silver *n*-alkanethiolates in most solvents and polymer precursors, makes it difficult to use this reaction for the in situ generation of a uniform dispersion of Ag NPs inside a coating. A possible solution arises from the use of a polymer con-

taining pendant alkyl chains in its structure such that the local hydrophobic domains can promote the uniform dispersion of the *n*-alkanethiolate salt. We recently showed that the luminescent Au(I) *n*-dodecanethiolate could be dispersed in an epoxy matrix containing pendant dodecyl chains [19].

In this study we analyzed the possibility of dispersing silver *n*-dodecanethiolate (Ag-DDT) in an organic–inorganic hybrid matrix obtained by the polycondensation of the precursor shown in Fig. 1, and the generation of metallic silver by the thermal decomposition of the dispersed thiolate.

The hydrolysis and condensation of the terminal methoxysilane groups of the precursor leads to a bridged silsesquioxane containing covalently bonded inorganic and organic domains. The organic–inorganic hybrid matrix is nanostructured through the self-assembly of the organic bridges by the tail-to-tail association of alkyl chains [20]. In a previous study we analyzed the dispersion of gold NPs stabilized by alkyl chains in this matrix [21]. The polycondensation of the precursor together with solvent evaporation was carried out in the presence of the gold NPs. At the end of this process a strong segregation of the NPs at the surface of the coating was observed, forming hierarchically assembled fractal aggregates [21]. Therefore, a uniform dispersion of gold NPs in the hybrid matrix could not be obtained. In the present study we followed a different strategy. Instead of trying to disperse preformed Ag NPs, Ag-DDT was synthesized in a solution of the precursor leading to a colloidal dispersion. The state of dispersion of Ag-DDT in the coating obtained by solvent evaporation and polycondensation, and the transformations taking place during the thermal treatment were investigated using a variety of experimental techniques.

* Corresponding author. Tel.: +54 223 4816600x240; fax: +54 223 4810046.
E-mail address: williams@fi.mdp.edu.ar (R.J.J. Williams).

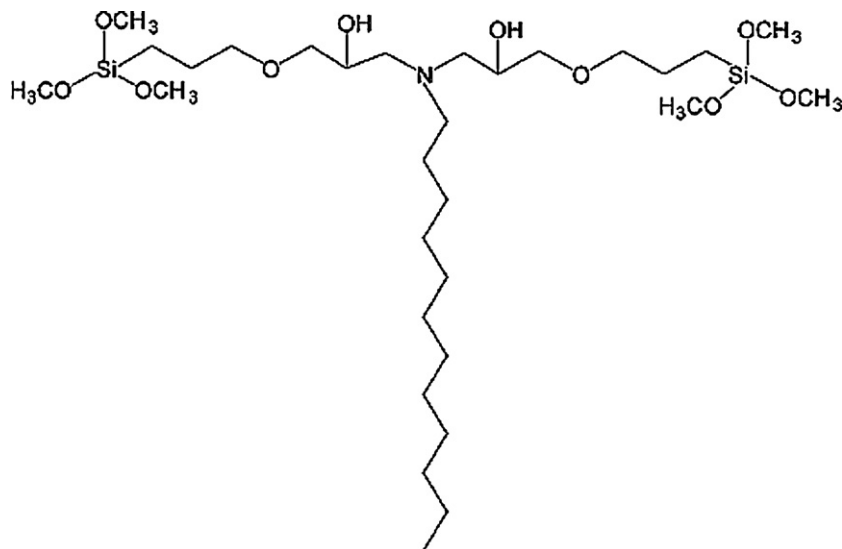


Fig. 1. Precursor of the organic–inorganic hybrid matrix.

2. Experimental

2.1. Dispersion of Ag-DDT in the organic–inorganic hybrid matrix

The precursor shown in Fig. 1 was synthesized following a procedure described in the literature [20,21]. Then, 2.5×10^{-3} moles of the precursor, 5×10^{-4} moles of *n*-dodecanethiol (Aldrich, 95% purity), and 5×10^{-4} moles of formic acid (88 wt% by weight), were dissolved in 25 mL of tetrahydrofuran (THF) using a glass recipient covered by an aluminum foil. In a following step 0.5 mL of a 1 M solution of AgNO_3 (QBS, 99% purity) were added to the THF solution with continuous stirring. The resulting colloidal dispersion was cast in a polyacetal recipient of about 5 cm diameter and placed in an oven at 308 K for 24 h. After this period, yellow films of about 500 μm thickness were obtained and removed from the polyacetal mold.

2.2. Thermal treatments

The films were subjected to thermal treatments in an oven held at 423 K for different periods of time: 30 min, 1 h, 4 h and 24 h.

2.3. Characterization techniques

X-ray diffraction (XRD) spectra were obtained in the 2θ range comprised between 2° and 60° (X'Pert Pro PANalytical diffractometer equipped with a graphite monochromator, proportional detector and a $\text{Cu K}\alpha$ radiation source).

Fourier-transformed infrared (FTIR) spectra were recorded with a Nicolet 6700 device (Thermo Scientific) in the absorbance mode, in the range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . Spectra were obtained by ATR employing 32 scans.

Differential scanning calorimetry (DSC) scans were performed with a DSC-50 Shimadzu equipment at 10 K min^{-1} .

Scanning electron microscopy images were obtained with different devices: JEOL JSM-6460LV SEM provided with an EDAX analyzer (Genesis Spectrum V5.11), Zeiss DSM 982 Gemini FEG-SEM microscope, and FESEM Zeiss Supra 40.

3. Results and discussion

3.1. Dispersion of Ag-DDT in the organic–inorganic hybrid matrix

Visual inspection of the films gave no evidence of a macrosegregation of Ag-DDT from the matrix. While the films without Ag-DDT were transparent and slightly yellow, those including Ag-DDT were opaque and yellow. The mass fraction of Ag-DDT dispersed in the coating was close to 10 wt%.

Ag-DDT forms lamellar crystals with a basic unit consisting of a nearly bidimensional inorganic layer locating S and Ag atoms, and all trans dodecyl chains extending perpendicularly (or with a small tilt angle) from the plane in opposite directions from alternating S atoms. The crystalline structure is formed by a tail-to-tail

association of dodecyl chains leading to a lamellar self-assembly of the basic units with a characteristic distance equal to 3.48 nm [14,22–24]. The presence of the characteristic lamellar structure of Ag-DDT embedded in the hybrid matrix was confirmed by X-ray diffraction spectra (Fig. 2).

The characteristic set of peaks corresponding to $(0k0)$ planes of the lamellar structure of Ag-DDT is observed for $k=1$ ($2\theta=2.41^\circ$) to $k=7$ ($2\theta=17.81^\circ$). The average distance corresponding to these peaks is 3.56 nm, in good agreement with the expected value. However, it must be pointed out that pendant dodecyl chains in the organic bridges of the hybrid matrix can also self-assemble by tail-to-tail associations. For the pure matrix only the first peak was observed in a similar position as the (010) peak of Ag-DDT [20,21].

The presence of Ag-DDT can be also assessed by determining the melting temperature of the crystals by DSC. The melting peak at 403.3 K (Fig. 3) is in excellent agreement with values reported in the literature [14,22,25–27].

FTIR spectra (not shown) were dominated by peaks of the matrix. The symmetric (d^+) and antisymmetric (d^-) stretching peaks of CH_2 groups of the pendant dodecyl chain of the organic bridge, were observed at 2851 cm^{-1} and 2919 cm^{-1} , indicating

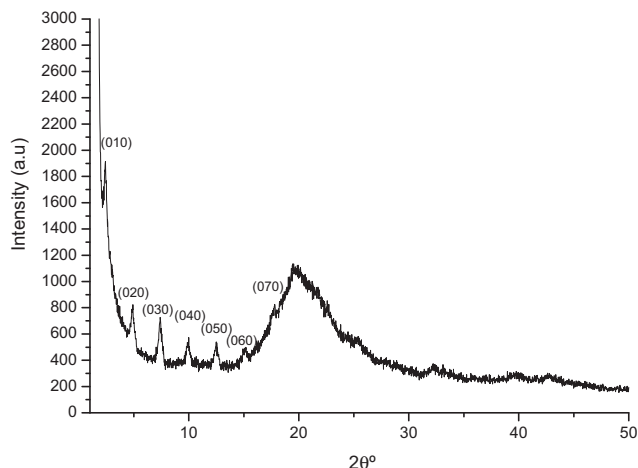


Fig. 2. X-ray diffraction spectrum of the hybrid matrix with embedded Ag-DDT.

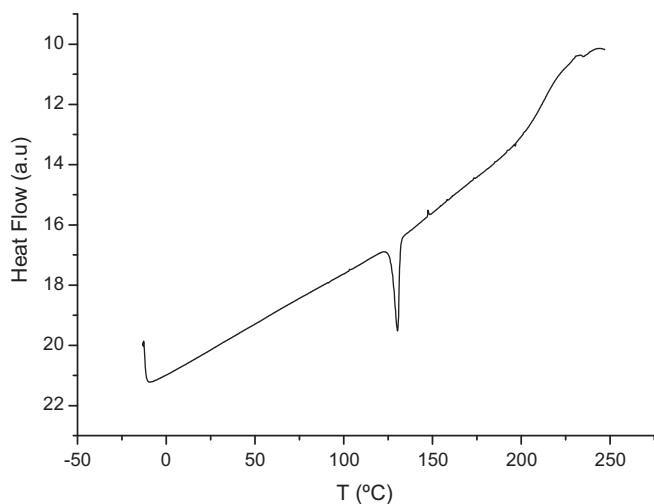


Fig. 3. DSC thermogram of the hybrid matrix with embedded Ag-DDT.

a relatively high fraction of trans conformations of alkyl chains [22,23,26,27].

3.2. Effect of the thermal treatment at 423 K

Heating the film for different periods of time at 423 K produced significant changes in its morphology. Fig. 4 shows SEM images of the surface of the initial film (a) and of the materials produced by heating 30 min (b), 1 h (c) and 4 h (d) at 423 K. SEM images of transversal sections of the films (not shown) were similar indicating that changes in morphologies were produced in the whole material.

As the hybrid matrix synthesized without Ag-DDT remained uniform with the same heating procedure, the microstructuration of the material must be driven by the presence of Ag-DDT.

A phase separation process took place slowly during the heating at 423 K. After 30 min heating, the micrograph shows the presence of entangled cylindrical domains dispersed in a non-structured (black) matrix. This microstructuration is more clearly evidenced after 1 h heating. After 4 h, the cylinders are packed into spiral-like structures dispersed in a non-structured medium.

EDAX was used to identify the overall composition of both domains. The non-structured matrix (black domains in the micrographs) showed the presence of Si, C and O but no evidence of S and Ag, indicating that they were constituted by the neat hybrid matrix. Inside the spirals Si, C, O, S and Ag were present, meaning that they were composed of structures containing both Ag-DDT and the hybrid matrix. When the area selected to perform EDAX was placed at the boundary of the spirals with the matrix, mostly C, S and Ag were observed, evidencing that Ag-DDT was highly concentrated in this region (Fig. 5).

A FESEM image of the bulk of one of the spirals is shown in Fig. 6. A layered structure is observed, presumably constituted by alternating layers of Ag-DDT and the bridged silsesquioxane. The linking unit among layers must be the dodecyl chains present in both structures.

The microstructuration of the material produced significant changes in the X-ray diffraction spectrum (Fig. 7). The 4-h heating at 423 K led to the transformation of the lamellar structure of Ag-DDT into a metastable crystalline structure characterized by main diffraction peaks at $2\theta = 16.83^\circ$ (A) (s) and 14.01° (B) (m), and small peaks at $2\theta = 12.39^\circ$ (C), 18.37° (D) and 25.45° (E) (w). This metastable crystalline structure of Ag-DDT is different from the hexagonal columnar mesophase found at high temperatures that exhibited a reversible transformation to the lamellar phase when

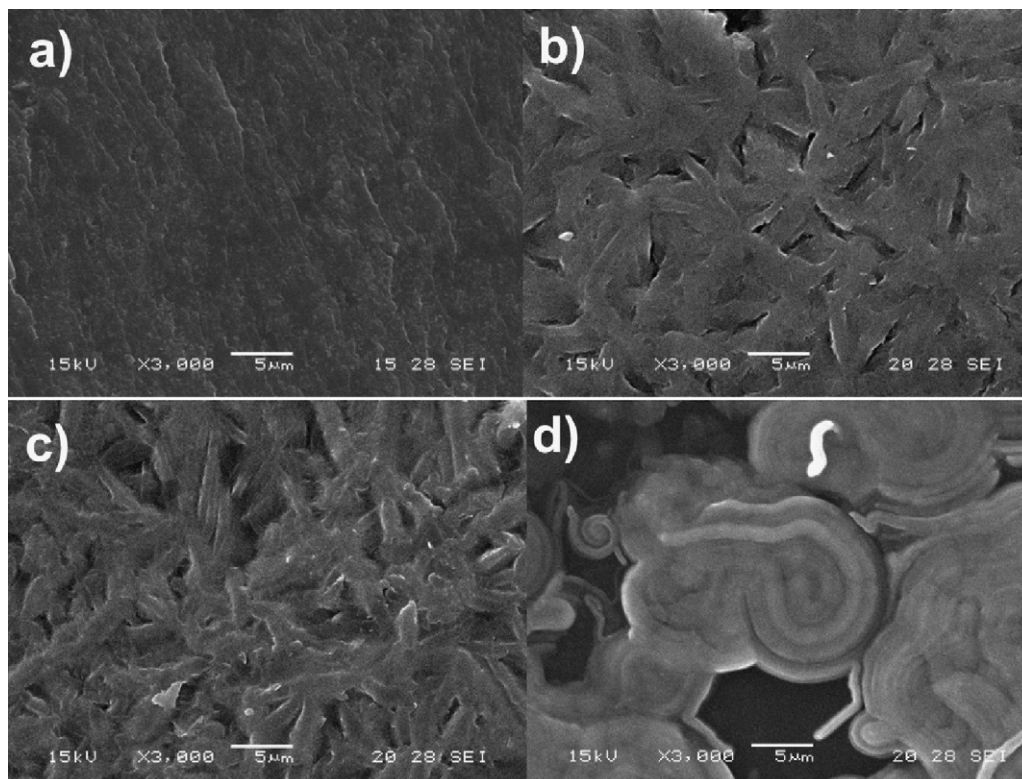


Fig. 4. SEM images of the initial film (a) and of the materials produced by heating 30 min (b), 1 h (c) and 4 h (d), at 423 K.

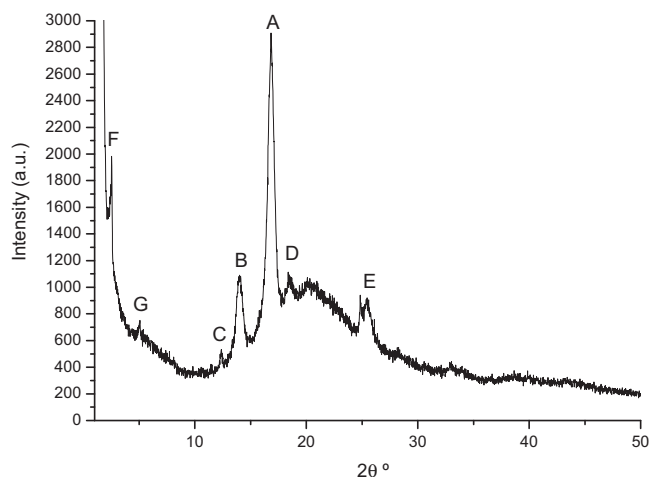
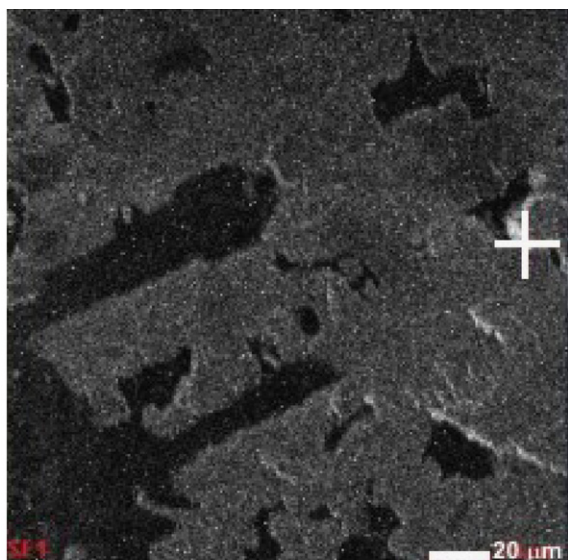


Fig. 7. X-ray diffraction spectrum of the material after 4 h heating at 423 K.

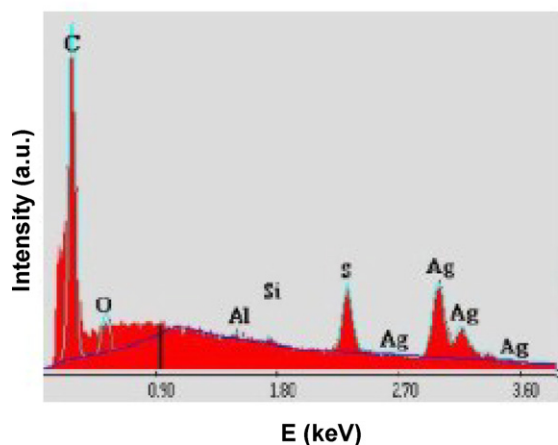


Fig. 5. Composition of the material located at the boundary of the spirals with black domains (SEM-EDAX).

cooling to room temperature [14,25]. In our case, the metastable phase that is reported for the first time here, was observed at room temperature instead of the stable lamellar phase. The peaks at 2.51° (F) (*m*) and at 5.07° (G) (*w*), are assigned to tail-to-tail associations of dodecyl chains. The metastable crystalline phase seems to act as a template for the orientation of the hybrid matrix, possibly by

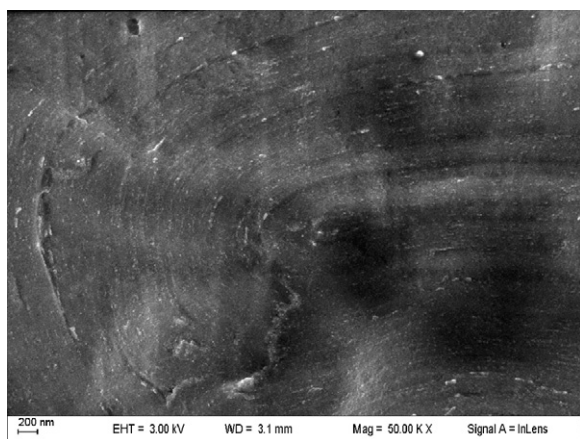


Fig. 6. FESEM image of the bulk of one spiral present in the material after heating 4 h at 423 K.

interaction among dodecyl chains present in both compounds. This gave place to layers of both components structured as large spirals in the micrometric range.

No significant changes produced by the 4-h heating were observed in FTIR spectra (not shown). Both the symmetric (d^+) and antisymmetric (d^-) stretching peaks of CH_2 groups of the pendant dodecyl chain of the organic bridge kept their initial values.

When the heating at 423 K was continued for 24 h metallic silver was produced by decomposition of the metastable crystalline phase. Fig. 8 shows an X-ray diffraction spectrum of the resulting product. Characteristic peaks of Ag(0) at $2\theta = 38.6^\circ$ and 44.6° , corresponding, respectively to (111) and (200) crystalline planes of cubic silver [16], are observed. The small peak at 10.8° (marked by an arrow) might be assigned to didodecyl sulfide or didodecyl disulfide [18], produced as by-product of metallic silver (Eq. (1)).

SEM images with two different degrees of magnification (Fig. 9) show dispersed domains of metallic silver generated after 24 h heating at 423 K. The low-magnification image (a) illustrates that silver domains are uniformly distributed in the whole material. The high-magnification image (b) shows a broad size distribution including some micrometric domains formed by self-assembled Ag NPs.

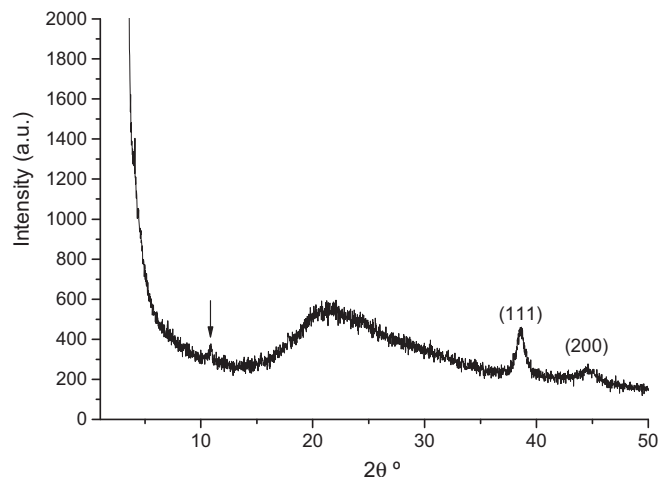


Fig. 8. X-ray diffraction spectrum of the material after 24 h heating at 423 K.

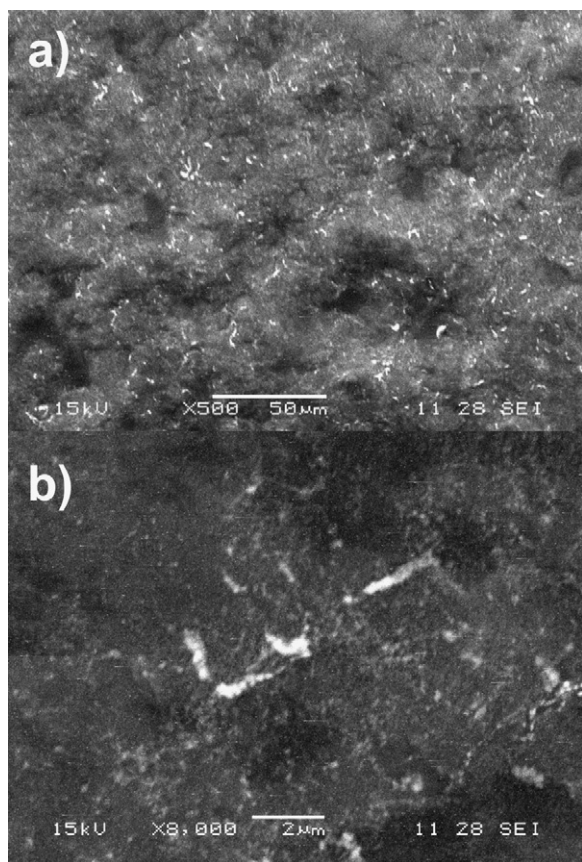


Fig. 9. SEM images with two different degrees of magnification showing dispersed domains of metallic silver generated after 24 h heating at 423 K.

4. Conclusions

The problem of producing a uniform dispersion of Ag-DDT in a solid matrix was overcome by synthesizing a colloidal solution of Ag-DDT in a solvent containing a precursor of a bridged silsesquioxane containing a pendant dodecyl chain. The polycondensation of the precursor together with solvent evaporation led to a uniform dispersion of Ag-DDT crystals in the organic–inorganic hybrid matrix. The thermal treatment of the material at 423 K led to the formation of a metastable crystalline phase of Ag-DDT that acted as a template for the orientation of the hybrid matrix into large spirals that were phase-segregated from the neat non-structured hybrid

matrix. Further heating at the same temperature produced the self-reduction of Ag-DDT leading to metallic silver domains with a broad range of sizes, dispersed across the whole material.

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