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Growing and stabilizing metallic nanoparticles inside mesoporous oxide thin films

M. Mercedes Zalduendo, Paula Y. Steinberg, Rusbel Coneo-Rodríguez, Andrea V. Bordoni, Paula C. Angelomé*
Gerencia Química & Instituto de Nanociencia y Nanotecnología, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, CONICET, Av. Gral. Paz 1499, San Martín (1650), Buenos Aires, Argentina

Corresponding author's email address and Twitter handle

angelome@cnea.gov.ar
twitter: @pcangelome

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Hybrid materials
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Sensors
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Abstract

Metallic nanoparticles (NPs) have interesting size-dependent optical properties and a high surface to volume ratio that make them appealing for many different applications, such as sensing, catalysis, energy conversion and storage, biomedicine, etc. These applications require avoiding NPs degradation, coarsening and/or aggregation. The use of porous templates has become a promising strategy to attain this objective. In particular, ordered mesoporous oxides prepared by sol-gel reactions combined with supramolecular templates are highly appealing supports, due to their high specific surface and regular and accessible porosity. Moreover, if these oxides are prepared as thin films, the manipulation and integration in portable devices is straightforward.
In this work, different alternatives to obtain metallic NPs stabilized within mesoporous oxide thin films are discussed. Firstly, the major effect of mesoporous TiO_2 thin films pores ordering over the amount and distribution of Au NPs obtained within is presented, along with the discussion of the architecture effect over the materials sensing capabilities.
Afterwards, the use of hybrid mesoporous thin films containing carboxylic and phosphonate groups as templates to form and stabilize Cu and Ag nanoparticles is presented. In all cases, the key effect of the surface chemistry over synthesis of the composites and their applications is highlighted.

Figures and tables

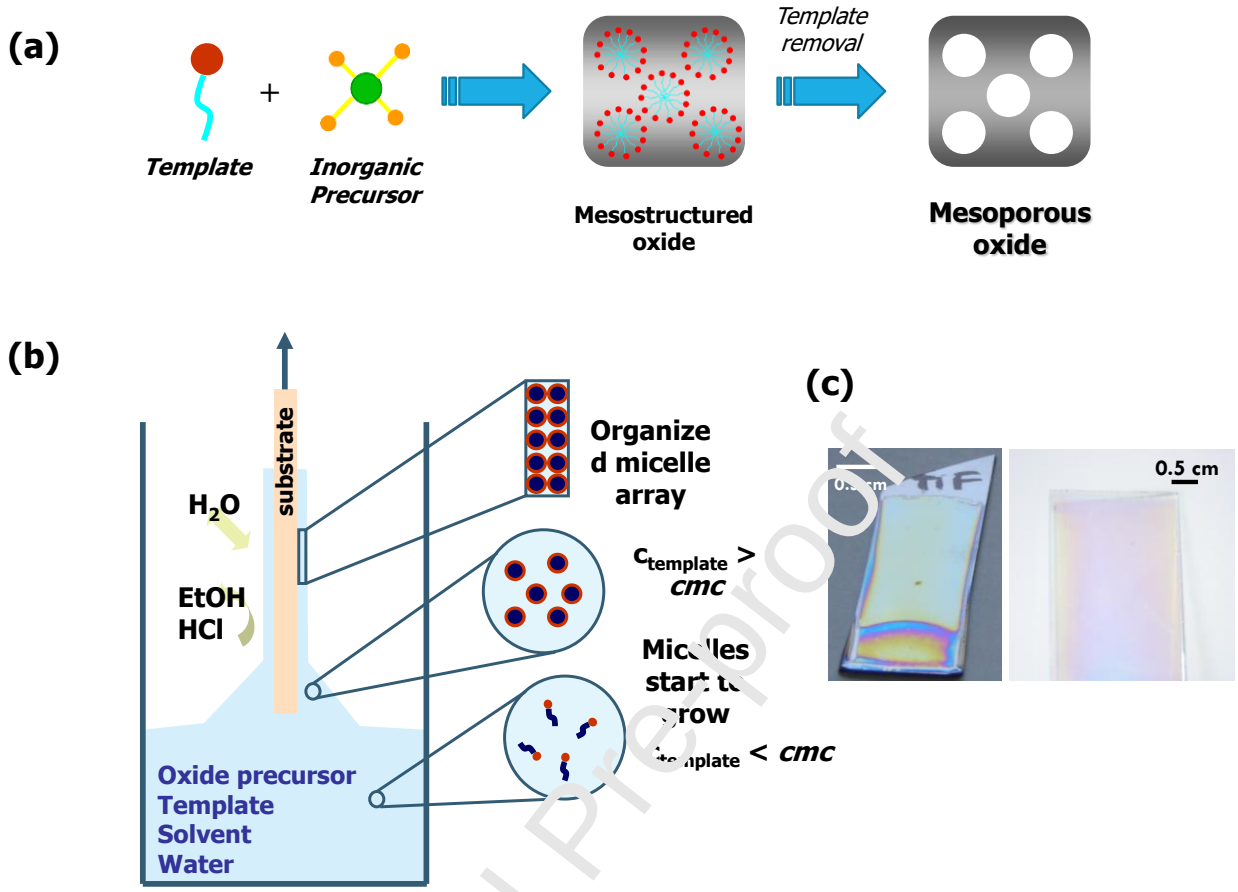

Figure 1 (a) Schematic representation of the reagents and steps involved in the production of mesoporous oxides. **(b)** Schematic representation of the *Evaporation Induced Self Assembly* process used to obtain mesoporous thin films. **(c)** Images of mesoporous TiO_2 thin films prepared onto silicon and glass coverslips.

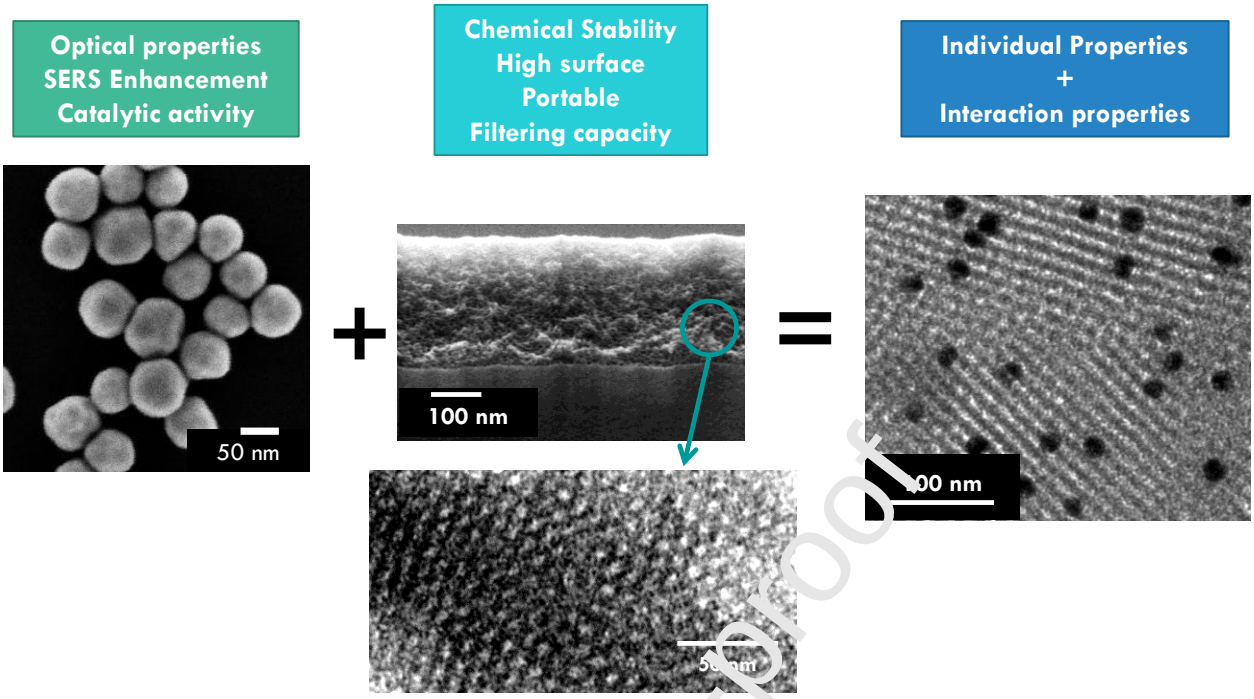

Figure 2: Main characteristics and electronic microscopy images of metallic nanoparticles, mesoporous thin films and composites containing both of them.

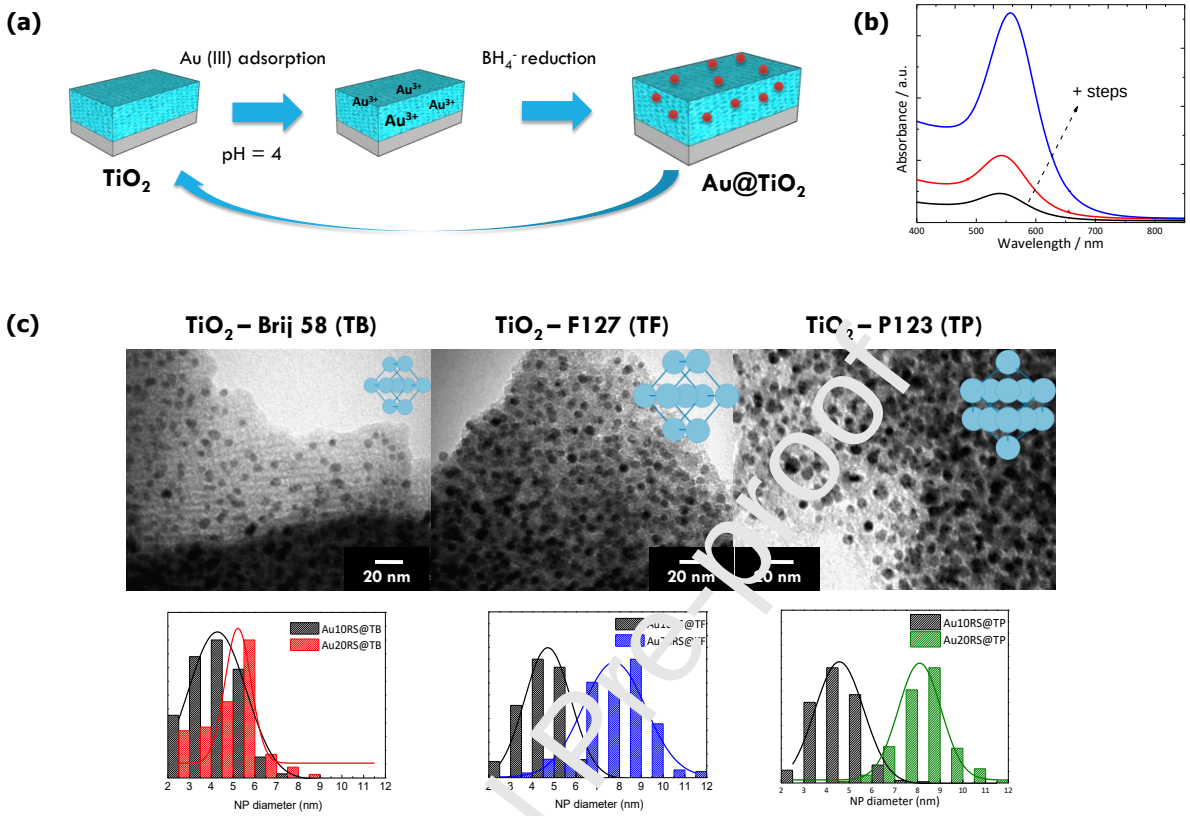

Figure 3 (a) Schematic representation of the adsorption-reduction method used to produce Au NPs inside mesoporous TiO_2 thin films. **(b)** UV-vis spectra of the obtained composite materials, as a function of the number of adsorption-reduction steps. **(c)** TEM images and NPs size histograms of different composite materials based on Au nanoparticles and mesoporous TiO_2 thin films, as indicated in the labels (*inset:* scheme of the pore ordering). *x*RS indicates the amount of adsorption-reduction steps used to produce the material.
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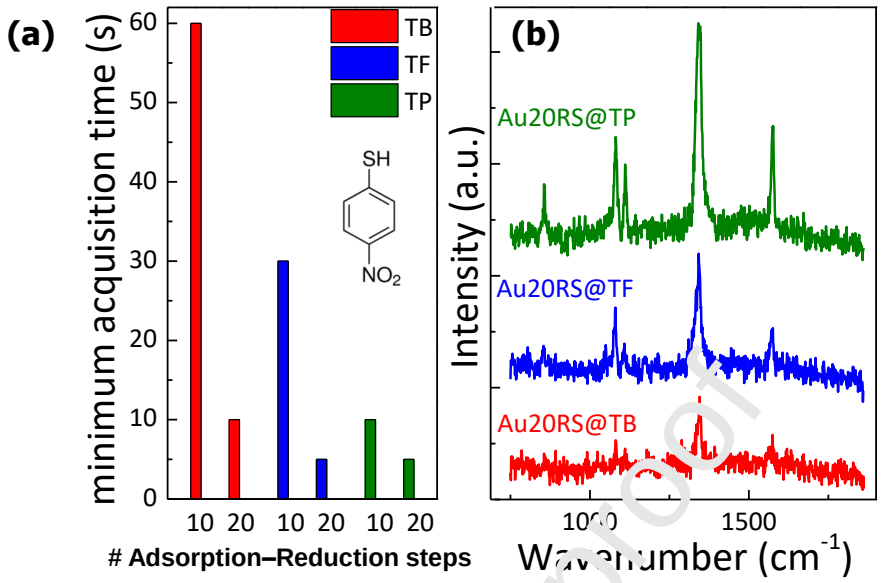

Figure 4 (a) Minimum acquisition times required for the detection of *p*-nitrothiophenol Raman probe (shown as inset) using different composite samples (see Figure 3) and **(b)** SERS spectra for *p*-nitrothiophenol using the samples indicated in the labels (acquisition time: 10 seconds). Each spectrum is the average of 4 spectra taken at 4 different points.
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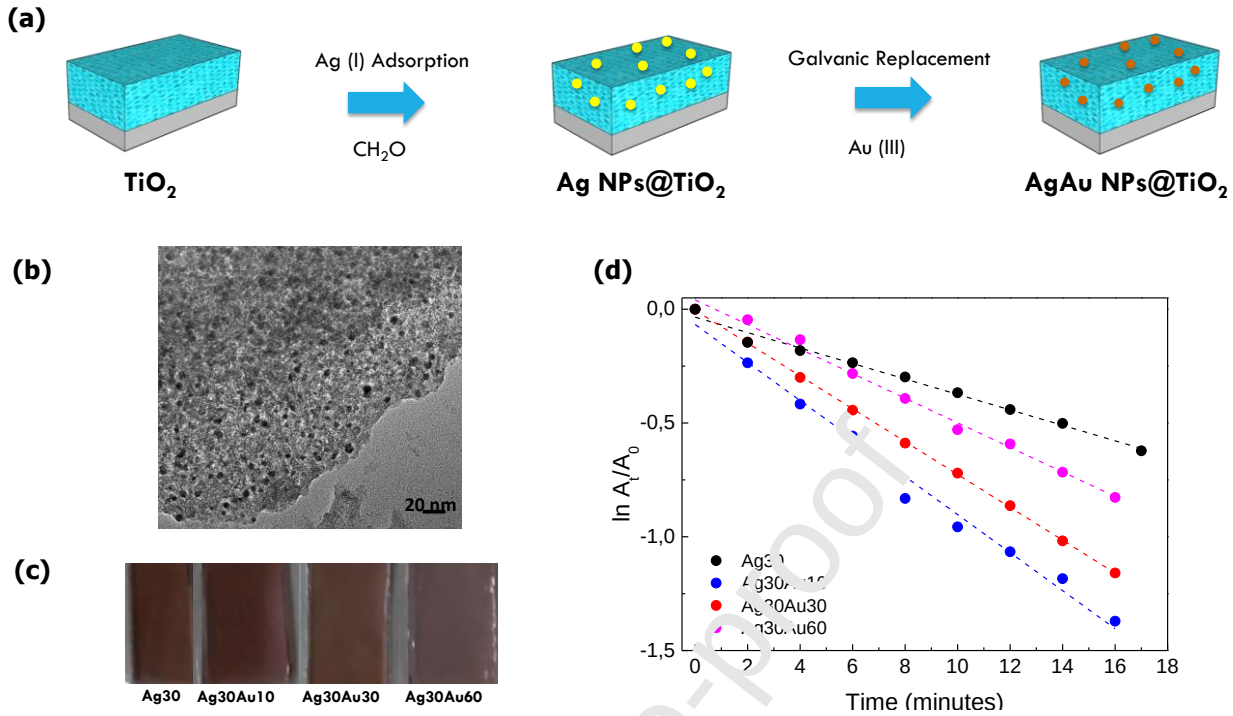

Figure 5 (a) Schematic representation of the galvanic replacement method used to produce Au-Ag bimetallic NPs inside mesoporous TiO_2 thin films. **(b)** Representative TEM image of the obtained samples. **(c)** Optical images of the samples. **(d)** Plot of ln (A_t/A_0) as a function of time for the 4-nitrophenol reduction reaction catalyzed by different composite materials, indicated in the labels. For (c) and (d): Ag30 = sample with Ag nanoparticles, Ag30Au*x* = saples with bimetallic nanoparticles, obtained changing the galvanic replacement time (*x*).

Adapted from DOI: 10.1002/ejic.201901186.

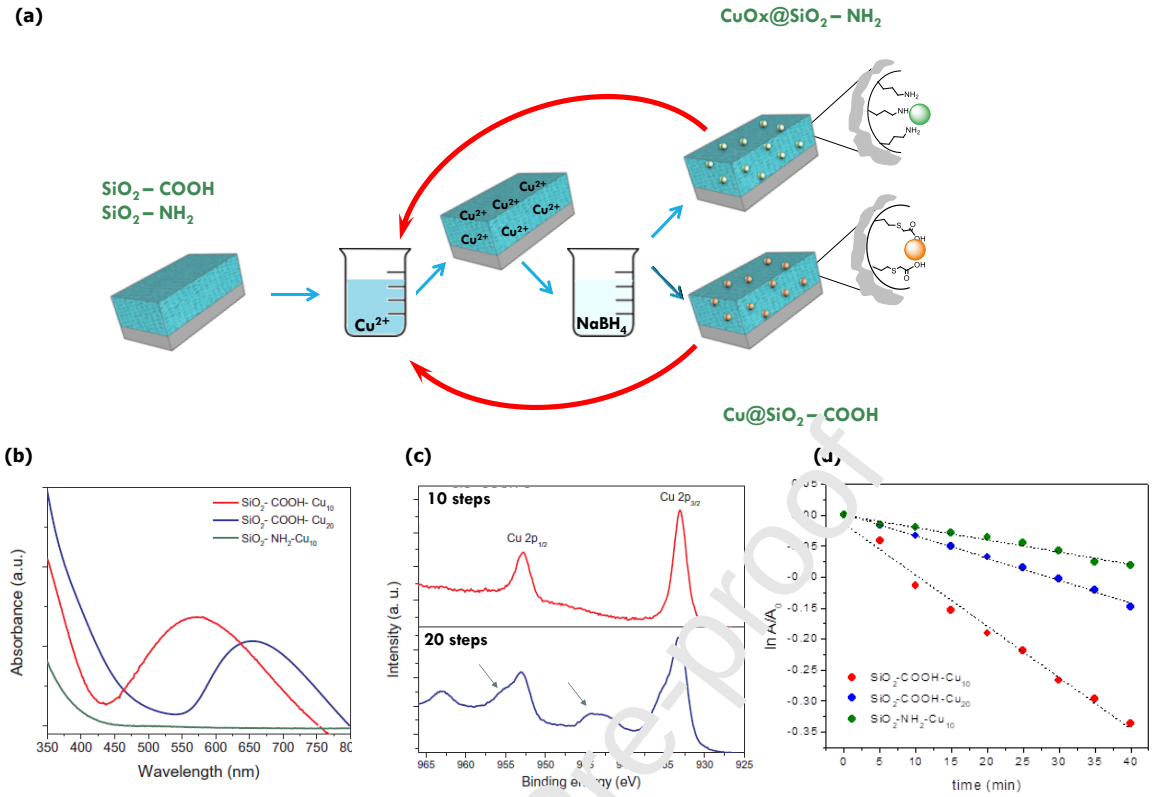

Figure 6 (a) Schematic representation of the synthetic method used to produce Cu NPs inside mesoporous thin films functionalized with COOH and NH_2 groups. **(b)** UV–vis spectra of different samples obtained using the method schematized in (a), as indicated in the labels. **(c)** XPS spectra in the Cu region for samples based on COOH modified silica prepared using different amounts of adsorption/reduction steps. **(d)** Plot of ln (A_t/A_0) as a function of time for the 4-nitrophenol reduction reaction catalyzed by different composite materials, indicated in the labels. The lines correspond to linear fitting of the data.

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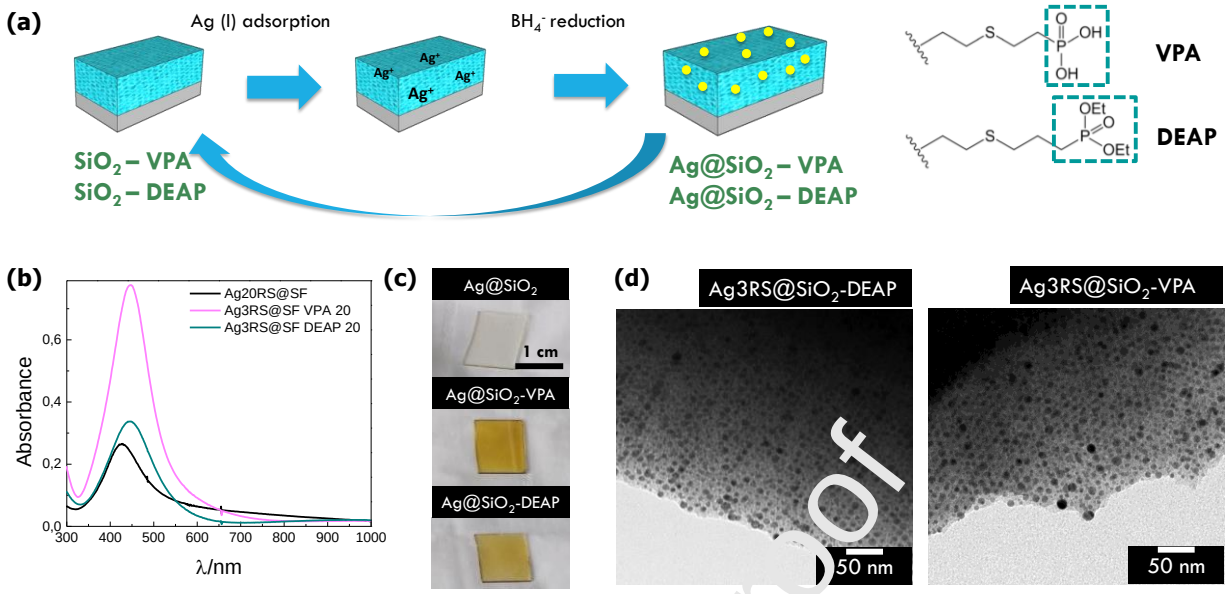

Figure 7 (a) Schematic representation of the synthetic method used to produce Ag NPs inside mesoporous thin films functionalized with phosphonate groups and their chemical structure. **(b)** UV-vis spectra, **(c)** optical images and **(d)** TEM images of selected samples, as indicated in the labels.

Adapted from *Microporous Mesoporous Mater.* **2020**, *295* Bordoni, A. V.; Zalduendo, M. M.; Escobar, A.; Amenitsch, H.; Moya, S. E., Angelomé, P. C., Phosphonate mesoporous hybrid thin films: Synthesis of organophosphosilane by thiol-ene click chemistry and applications in formation and stabilization of silver nanoparticles. 109958, Copyright (2020), with permission from Elsevier.

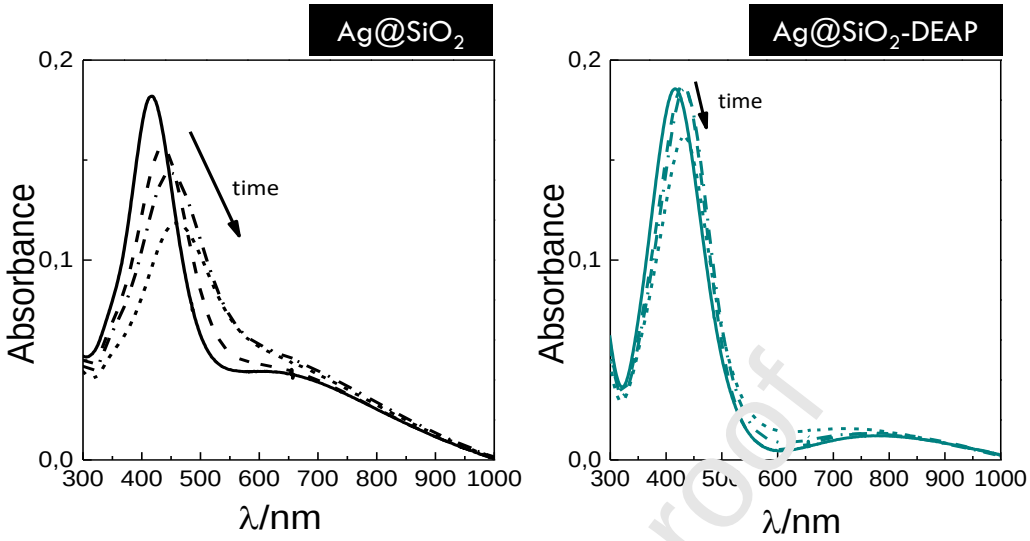

Figure 8 UV–vis spectra of different composite materials (indicated in the labels) as a function of aging time. Changes are more noticeable in the composite sample that does not include phosphonate groups.
Adapted from *Microporous Mesoporous Mater.* **2020**, *295* Bordoni, A. V.; Zalduendo, M. M.; Escobar, A.; Amenitsch, H.; Moya, S. E.; Angelomé, P. C., Phosphonate mesoporous hybrid thin films: Synthesis of organophosphosilane by thiol-ene click chemistry and applications in formation and stabilization of silver nanoparticles. 109958, Copyright (2020), with permission from Elsevier.

CRediT author statement

M. Mercedes Zalduendo: Investigation, Data Curation, Writing- Original draft preparation **Paula Y. Steinberg:** Investigation, Data Curation, Writing- Original draft preparation**, Rusbel Coneo-Rodríguez:** Investigation, Data Curation, Writing- Original draft preparation**, Andrea V. Bordoni:** Conceptualization, Data Curation, Investigation, Funding acquisition, Writing- Original draft preparation**, , Paula C. Angelomé:** Conceptualization, Data Curation, Project administration, Funding acquisition, Writing- Reviewing and Editing.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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