A silica-silver nanocomposite obtained by sol-gel method in the presence of silver nanoparticles

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Abstract: Silver nanoparticles (AgNPs) were obtained by a redox reaction, using a glucose-containing cyclosiloxane as a reduction agent and stabilizer. Then the AgNPs aqueous solution was used as the reaction medium for the sol-gel process, starting from tetraethylorthosilicate (TEOS) as silica precursor. The nanocomposite material resulted (SilAg) after solvent removal, aging and calcination and was investigated by infrared spectroscopy (FT-IR), atomic force microscopy (AFM), scanning electron microscopy coupled with energy dispersive X-ray system (SEM/EDX), transmission electron microscopy (TEM), energy-dispersive X-ray fluorescence spectroscopy (EDXRF), X-ray diffraction (XRD) and dynamic vapor sorption (DVS). The results were compared to model silicas obtained without silver. A higher condensation degree in SilAg was obtained due to the basic medium used in the first step and was confirmed by a sorption capacity lower than for the model silicas. The solid surface area calculated with GAB analysis using DVS data for the water vapors is 210 m² g⁻¹. The nanocomposite showed good catalytic activity for hydrogen peroxide decomposition.

Keywords: Silver nanoparticles • Siloxane surfactant • Sol-gel • Silica

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1. Introduction

Nanostructured materials, including mesoporous silica [1], metal oxides and their nanocomposites [2,3] or noble metal nanoparticles [4] have been intensively studied in the last decade.

One class of materials that clearly emerged are metal-containing nanocomposites based on silica. The morphology of such nanomaterials is diverse. They have been prepared and investigated as metal core-silica shell nanoparticles, nanolayers, tri-component nanocomposites, and silica core-metal coating colloids. The developments in this field are based on quite a few interesting characteristics that have been demonstrated. Metallic nanoclusters embedded in dielectric matrices have unique optical and magnetic properties. For example, Ni–Pt/SiO₂ supported alloyed clusters exhibit enhanced magnetization, while Pt favors the nickel reduction yield [5]. Metallic-dielectric nanocomposite layers with excellent electron field emission properties have been obtained by an ion implantation technique [6]. Trilayer Ag/SiO₂/Ag plasmonic thermal emitters have been prepared and analyzed [7]. Silver core-silica shell nanoparticles with various shell thicknesses featuring a variety of fluorophores have demonstrated their applicability for metal-enhanced fluorescence (MEF) and single nanoparticle sensing [8]. For these applications, silver nanoparticles (AgNPs) were obtained and coated with silica and then the fluorophores were doped or covalently linked onto the silica surface. It has been shown that AgNPs were responsible for important enhancements for fluorescence signal and particle detectability. Uniform and dispersed upconversion nanoparticles (Ag@SiO₂@Y₂O₃:Er) based on a core/spacer/shell approach were reported to increase the photoluminescence performance in biological and nanophotoelectronic applications. In essence, AgNPs are able to enhance the luminescence of rare-earth
ions when included in such complex structures [9]. Surface enhanced Raman scattering (SERS) performed in colloidal dispersions of noble metals is well known as a highly sensitive tool for the molecular detection and characterization of wide range of chemical and biological agents up to single molecular concentration levels. Ag clusters on silica colloidal nanoparticles, as well as Ag core-silica shell nanoparticles showed this effect [10,11].

The most commonly used method to prepare silica-silver nanocomposite particles is based on the fabrication of SiO2 microspheres, the surface functionalization of the SiO2 substrates with silane coupling agents, and the deposition or formation of Ag nanoparticles onto the functionalized silica substrates [12]. Silver clusters on silica colloidal nanoparticles in aqueous suspension where also prepared by laser irradiation [10]. The sol-gel method is widely used for the preparation of silica-silver nanocomposites, due to its versatility and low cost [13]. Silver and gold silica nanocomposites were manufactured since the 90s by combining gama irradiation with the sol-gel process [14,15]. Porous silica with AgNPs dispersed within its pores has been reported showing optical memory effect [16].

Heterogeneous nanocomposite materials containing at least one metal have catalytic properties that differ dramatically from those of their single components. The application of Ag-SiO2 nanocomposites as catalysts has gain great interest during the last few years. SiO2 is used either to support the silver catalyst or to enhance the catalytic activity of a third component. Some examples of highly efficient catalytic activity of Ag/SiO2 are hydrogenation reactions [17], hydrogen peroxide decomposition [18], selective oxidation of alcohols, oxidation of CO [19], and reduction of nitrogen oxides [20].

Ag-SiO2 co-doped TiO2 film obtained by sol-gel has potential applications for self cleaning and antibacterial ceramic tiles [21]. It was found that doped silver increases the photosensitivity and photocatalytic properties of TiO2, with the effect being influenced by the silica shell thickness [22].

In our group, we were interested in the different materials obtained by the sol-gel method [23-25] and new approaches for nanoparticles [26,27]. We have described the synthesis of the silver nanoparticles (AgNPs) using a glucose-modified siloxane surfactant as the stabilizer and the reducing agent [28]. Here we report a simple and effective way to synthesize Ag-SiO2 nanocomposite, by combining the same method for preparing AgNPs with the sol-gel generation of silica, in water.

2. Experimental procedure

2.1. Materials

Tetraethylorthosilicate (TEOS) was purchased from Fluka. The glucose-modified cyclosiloxane (DSG) (Scheme 1) was obtained according to the procedure described in [29].

Tollens reagent [Ag(NH3)2OH] has been prepared prior to utilization, using the standard procedure.

Fumed silica, Aerosil 380 (Degussa), specific surface 380 m² g⁻¹, particle diameter 0.003 – 0.015 μm was used as received.

2.2. Measurements

The infrared spectra were registered on a Bruker Vertex 70 FT-IR instrument, in transmission mode, in the 400-4000 cm⁻¹ range (resolution 2 cm⁻¹, 32 scans), at ambient temperature.

The AFM measurements were made on a SPM Solver Pro-M platform (NT-MDT, Rusia), in air, in semi-contact mode, using a rectangular NSG10/Au cantilever with a nominal elasticity constant Kₙ = 11.5 Nm⁻¹. Drops of the reaction mixture were placed on glass slides and slowly dried at room temperature prior to analysis.

For SEM studies, samples were cast on glass slides and dried at ambient temperature, then the glass slides were fixed on copper supports. The surface was examined with an Environmental Scanning Electron Microscope (ESEM) type Quanta 200, operating at 20 kV with secondary electrons. The microscope is equipped with an Energy Dispersive X-Ray system (EDX) for qualitative and quantitative analysis and elemental mapping.

The presence and ratio of Ag and Si were determined using an Energy-Dispersive X-ray Fluorescence (EDXR) system EX-2600 X-Calibur SDD.

The TEM investigation was performed with Hitachi High-Tech HT7700 Transmission Electron Microscope.

Wide angle X ray diffraction (WAXD) measurements were performed using a Bruker D8 ADVANCE Diffractometer, using the Ni-filtered Cu-K alpha radiation (λ = 0.1541 nm).

The sorption capacity of the water vapors was measured in a dynamic regime at 25°C (298 K) in the relative humidity (RH) range between 0-90% by using an IGAsorp equipment (Hiden Analytical, Warrington UK). The vapor pressure was increased and decreased after an established program (“Prog1”), in 10% humidity steps between 0 and 90% RH for sorption and reverse for desorption, each having a pre-established equilibrium time between 70 and 80 minutes. The percent of the weight gained was calculated with the formula:
In order to calculate the rate of drying ($R_d$), the rate of wetting ($R_w$), and the equilibrium state ($R_w = \text{Maximum weight gain / equilibrium time} (t_w)$). After that, the samples were kept at RH=0% in nitrogen flow, until the weight remained constant ($R_d = \text{Total weight loss / equilibrium time} (t_d)$).

2.3. Preparation of the model silica Sil0 and Sil1

TEOS (0.5 mL) and water (10 mL) -for Sil0- or TEOS and an aqueous solution of D5G (10 mL, 0.36 g L$^{-1}$) –for Sil1- were mixed together. The two-phase mixture was stirred at 80°C for 2 h, then at room temperature for 20 h. Within this time, the sol phase was formed. The solution was then poured into a Teflon dish to allow for the evaporation of ethanol and water. The crude silica formed was extracted with water then dried at 120°C for 2 h. Subsequent thermal treatment consisted of heating at 700°C to a constant weight. For AFM measurements, samples were cast on glass slides directly from the reaction mixture, left to dry and then rinsed with water and dried again.

2.4. Preparation of the silica-silver nanocomposite SilAg

The procedure described in [28] for the preparation of silver nanoparticles without adding glucose has been used, as follows. The silver complex (4 mL), containing around 1.8 g Ag L$^{-1}$ (approx. 6.6×10$^{-5}$ mol Ag$^+$) was added under pressure to 15 mL of a 0.36 g L$^{-1}$ D5G aqueous solution, the mixture was heated at 50°C for 1 h, and then left at room temperature for 1 day. The yellow solution was used for the preparation of silica-silver composite. TEOS (0.5 mL) and the silver nanoparticle solution were mixed together for 1 h, heated at 80°C for 2 h then stirred at room temperature for another 24 h. The resulted sol was treated similarly with the model silicas. The crude silica was a grey powder, while the final material, after calcination was white with a faint ochre shade.

2.5. Test of catalytic activity

Catalytic tests were done on hydrogen peroxide decomposition, in alkaline solution, using the gasometric technique [30]. In this reaction, the H$_2$O$_2$ is present as perhydroxyl ion and oxygen evolves from the vessel, according to the equation:

$$2\text{HO}_2^- = \text{O}_2 + 2\text{OH}^-$$

The O$_2$ formed displaces the water from a Bunte gas burette and its volume is measured versus time, under atmospheric pressure and at 300 K. A 4N NaOH solution (50 mL) and the catalyst (10 mg) were mixed together for 15 min, and then 5 mL of 15% H$_2$O$_2$ was added the oxygen evolution was monitored in time.

3. Results and discussion

In a previous paper [28] we have discussed the role of a glucose-modified cyclosiloxane (D5G, Scheme 1) as stabilizer as well as reduction agent in the synthesis of AgNPs. We have shown that this compound is able to stabilize AgNPs when used in very small amounts. On the other hand, the kinetics of the silver ions reduction was studied, using glucose as reducing agent or with no glucose added, when the stabilizer participates in the reaction, thereby allowing the formation of Ag within a much longer time.

Here we investigate the possibility of obtaining a silica-silver nanocomposite using preformed nanoparticles dispersed into the surfactant solution, and with TEOS as a silica precursor. For the synthesis of AgNPs we used the approach where no other reduction agent but the surfactant is used. The AgNPs resonance plasmon was confirmed with a UV-Vis measurement at 420 nm. Based on our previously reported data, the estimated average diameter of the AgNPs obtained with this procedure is between 8 and 14 nm [28]. The TEOS was added to this nanoparticles solution, and the silica formed after the removal of water. Subsequent calcination gave the silica-silver nanocomposite, SilAg. The same reaction was performed using only the D5G solution, in order to obtain silica without silver in similar conditions (Sil1). A silica obtained in water, without any catalyst or surfactant was also taken as a reference - Sil0-

In Fig. 1, the FT-IR spectrum of crude silica-silver material before calcination is presented, with an emphasis on the main modifications that occurred after the thermal treatment (insert). The formation of the silica network is assessed by the absorption bands centered at 1100, 800 and 470 cm$^{-1}$, which are assigned to the asymmetric and symmetric vibrations of Si-O-Si linkage in SiO$_2$ [13,16]. The bands centered at 3463 cm$^{-1}$ and 1637 cm$^{-1}$ correspond to stretching and bending vibrations of the bound water molecules [13]. These are the main absorption bands that appear in all the synthesized materials. The band at 1385 cm$^{-1}$ in SilAg was assigned to the silver clusters. According to some
data [13] the Si-O-Ag stretching is considered to appear at around 600 cm\(^{-1}\); so the weak band at 554 cm\(^{-1}\) in our spectrum could indicate this bond. According to other reports [19] the incorporation of metal into the silica framework is shown by the stretching vibration of the Si–O–Me linkage located at 960–970 cm\(^{-1}\), but in our case this band appeared also in the model silicas, which do not contain metal.

The band at 971 cm\(^{-1}\) was assigned to the stretching vibrations of Si-O-H groups and shows a rather low condensation in the silica-silver sample before calcination. The IR spectra of the crude model silicas (not shown) showed a more pronounced -OH bands. The presence of the un-condensed Si–OH groups in this stage is normal, since TEOS undergoes a hydrolysis-condensation process in water and subsequently in atmosphere and with no condensation catalyst. It is known that the kinetics and morphology of the silica networks strongly depend on the reaction conditions and especially on the pH value [31]. In our case, the model reactions occurred in water or in the presence of a nonionic surfactant and at a neutral pH, while the nanocomposite was formed in a basic medium (pH = 8.5), due to the Tollens reagent used for AgNPs. Consequently, the condensation step in SilAg was more rapid and to a higher degree than in the model reactions. After calcination, the medium band at 971 cm\(^{-1}\) in SilAg remained as a shoulder (Fig. 1, insert), which means that complete condensation did not occur even after the thermal treatment and this is due to a lack of mobility in the formed silica framework. On the other hand, the bands at 3460 cm\(^{-1}\) and 1637 cm\(^{-1}\) remained after calcination, showing that the absorption of water due to uncondensed silanol groups is still important. The weak band at 554 cm\(^{-1}\) becomes a shoulder after calcination and can be assigned to the Si-O-Ag linkages. This would mean that they break on heating, and silver involved in these bonds is reduced by thermal treatment.

Under our experimental conditions, the formation and subsequent reduction of silver oxide on the surface of the initial AgNPs cannot be excluded because oxidation of silver is thermodynamically favored at room temperature [32]. The synthesis occurred in three steps: 1) formation of AgNPs (yellow solution); 2) formation of silica in the presence of AgNPs in atmosphere (grey powder); 3) calcination at 700°C, which resulted in white-ochre material. The change of color from the initial yellow of AgNPs to the grey in the crude silica indicates oxidation of silver during the second step of the process. However, Ag\(_2\)O decomposes above 280°C, which explains the second change in color, which is due to a reduction of silver during the thermal treatment. This effect was observed by others and attributed to the initial formation and subsequent decomposition of Ag\(_2\)O on the surface of Ag particles in different ambient conditions [16]. As expected, the final color of the material indicates the presence of AgNPs in a small amount. Although the complete absence of a trace of a byproduct cannot be claimed, all our data point towards silica-silver nanocomposite as the main material, and will be discussed later.

For example, no evidence of organic material is observed in the FT-IR spectrum, even in the crude silica (observe the C-H region at 2850-3000 cm\(^{-1}\) in Fig. 1). In fact, the amount of D5G used was very low (about 5.4 mg reported to 0.5 mL of TEOS), and it was extracted with water in the workup step, therefore (if present) traces of surfactant were undetectable. It is worth mentioning that the surfactant decomposes below 700°C. As expected, the –OCH\(_2\)-CH\(_3\) groups were also absent in the FT-IR spectrum, showing that the hydrolysis process of the silica precursor was completed, and the formed ethanol was efficiently removed.

The AFM images of SilAg and Sil1 precursor materials before calcination are presented in Fig. 2. The AFM images from both samples indicate the formation of silica particles in this step. In crude SilAg, monodisperse nanoparticles of around 20 nm were observed, while in crude Sil1 the particles are larger, and not uniform in size.

The SEM analysis (not shown) presented similar information about the samples before calcination. The EDX system coupled with the scanning electron microscope revealed the presence of silver in SilAg (Fig. 3). The other elements were present in small amounts and are due to the glass support. As previously mentioned, C was not detected in the EDX spectrum, supporting the absence of organic material. The X-ray fluorescence spectrometry was also used to detect the presence of Si and Ag in the sample. The atomic ratio between Si and Ag was calculated from the
The XRF spectrum, and the value obtained is close to the theoretical value (34 vs. 37). This indicates about 5% Ag (wt.) in the silica.

The SilAg sample was further analyzed by TEM after calcination. The image in Fig. 4 shows that subsequent to the thermal treatment, the silica particles observed initially by AFM transformed into a thin film, with embedded silver nanoparticles of 7-8 nm. The associated electron diffraction pattern indicates a certain crystallinity of the sample. The TEM images didn’t show a porous structure, but rather a monolith film aspect of the calcined sample.

The XRD analysis showed a crystalline sample. As can be observed in the diffraction diagram (Fig. 5), in the wide angle region, pronounced diffraction peaks are present. These results are summarized in Table 1.

**Figure 1.** FTIR spectrum of the SilAg precursor before calcination; insert-region of interest before and after calcination.

**Figure 2.** AFM images (2D, 3D and phase, respectively) of the SilAg precursor (a-c) and Sil1 precursor (d-f).
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According to [33] the main peaks can be assigned to a crystalline form of silica, the cristobalite (Table 1). The main peak corresponding to d=2.35 Å can be assigned to the crystalline lattice of silver [34,35]. The small diffraction peaks at 2θ = 1.78° and 2θ = 4.5°, correspond to a structural periodicity (d) of 49.6 and 19.6 Å, respectively and may indicate the presence of small pores. There is no evidence in the XRD spectrum for Ag2O or other silver oxides, as compared with reported data [36,37]. This clearly shows that the final product, obtained after thermal treatment (SilAg) is a silica-silver composite.

In order to evaluate the behavior under different humidity levels of SilAg, water vapor sorption-desorption experiments were conducted, using Sil0 and Sil1, and commercial silica (Aerosil) as references. Before sorption measurements, the samples were dried at 25°C in nitrogen flow (250 mL min⁻¹) until the weight of the sample was in equilibrium at RH<1%. The sorption-desorption kinetics was evaluated following a step-by-step procedure (“Prog1” described in the experimental section) and the isotherms are presented in Fig. 6.

All prepared samples exhibit similar shape of the isotherms that can be described as type V under the IUPAC classification [38,39]. These are adsorption isotherms with hysteresis, characteristic for porous solids [40]. Capillary condensation, different mechanisms of filling and emptying the pores and many other possible causes may be the origins of the hysteresis [41]. Taking into account their shapes, the hysteresis except that of Sil1 could be associated with H2 type characteristic for the systems where the distribution of pore size and shape is not well-defined. Instead, the hysteresis of Sil1 seems to be very close to the type H1 characteristic for agglomerates of approximately uniform and regularly arranged spheres [42].

In Table 2, some characteristics of the calcined samples are presented and are based on sorption-desorption isotherms. Judging from the total water vapor sorption capacity, the samples differ significantly. The sorption capacity of SilAg is the lowest, and comparable with Aerosil, while Sil1 absorbs more than double the

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**Figure 3.** The EDX spectrum of the SilAg precursor, acquired with SEM/EDX system.

**Figure 4.** TEM image of the calcined SilAg sample.

**Table 1.** The diffraction peaks (2θ, degrees) detected in sample the SilAg (calcined).

| Assignment* | Primary | Secondary | Tertiary |
|-------------|---------|-----------|----------|
| Cristobalite| 21.99   | 36.18     | 31.43    |
| Silver      | 38.23   | 44.43     | 77.63    |

*After [33]
amount of humidity, even after calcination. This result shows again that SilAg has the highest condensation degree of the –OH groups. However, the hysteresis is significant due to the slower desorption in the high humidity region.

The rate of wetting and drying were calculated as the maximum weight gain or loss of the sample in extreme humidity conditions (90%, and 0% respectively) per time at equilibrium (“Prog2”). In all cases, there are significant differences between wetting and drying rate; generally drying occurs faster, which indicates a hydrophobic behavior. Again, the parameters calculated for sample SilAg are similar to those of Aerosil. It is worth mentioning that all the samples adsorbed more water with “Prog2”, and only part of the water gained at 90% RH was desorbed in the second step of the program, with the notable exception of Aerosil.

The GAB (Guggenheim-Anderson-de Boer) model was used to calculate the average pore size, the monolayer sorption values and the solid surface area from the desorption branch of the curves, assuming the pores have cylindrical shape. The GAB equation was chosen over the BET (Brunauer-Emmett-Teller) model, because it covers a larger range of humidity conditions.
A silica-silver nanocomposite obtained by sol-gel method in the presence of silver nanoparticles and it gave good fitting to the experimental data. The results of the GAB analysis indicate a surface area of 210 m² g⁻¹ for the SilAg nanocomposite, which is twice as high as for the model silica Sil0 and Aerosil. The calculated average pore size for SilAg is smaller than for the other silica materials prepared in this study, but again comparable with Aerosil. The average pore size calculated from DVS measurements (2.3 nm in radius) for SilAg is in good agreement with the XRD result, which showed periodicity parameters of 5 nm and 2 nm.

It is worth mentioning that usually literature data for these parameters are based on BET model and applied to liquid nitrogen adsorption isotherm [19,20,43]. Here, the calculations were made applying the GAB model for the water vapor sorption, aiming to compare the samples according to the same experimental procedure. Of course, thus obtained values cannot be compared accurately with those from N₂ sorption, especially due to different size of the adsorbed molecules and to the polarity of water molecules, which may develop interactions [44]. Taking a commercial silica as a reference may give a more objective evaluation, although the value thus obtained for Aerosil is significantly smaller than that indicated by the producer. In an early study [45] the methanol adsorption was used to study the porosity of Aerosil, and the methanol BET surface area at different temperatures was also found smaller than the value indicated by the producer. The authors also suggested that the Aerosil 200 investigated contained some mesopores, although it is considered a nonporous material. It is also possible that the intra-agglomerate pores were determined [46].

We tested the catalytic activity of SilAg in H₂O₂ decomposition in alkaline conditions and a good result was obtained, although the sample contains only about 5% silver. Our calculations gave a turnover number (TON) value of 547 reported to Ag (moles of H₂O₂ per mole of Ag) and turnover frequency (TOF) of 337 h⁻¹. It was rather difficult to find comparative data, but these may be considered high values. For example, TON values of 360-380 were reported for oxidation reactions with H₂O₂ (values calculated as moles of product per mol of catalyst) [47]. The catalytic epoxidation of olefins with H₂O₂ was reported to occur with TOF of max. 7 h⁻¹ [48]. Similar reactions with tert-butylhydroperoxide and a silica-supported metal complex as a catalyst gave TOF values of max. 59 h⁻¹ [49]. Of course, there are other factors that have to be considered when assessing the catalytic activity, like selectivity, yield, reaction conditions and so on. These studies will follow in the near future.

SilAg is a promising material, especially if we take into account the simple experimental setup, which makes use of very few materials and un-sophisticated technique. The key element may be considered the glucose-modified cyclosiloxane, D₅G, which is very effective in producing and stabilizing AgNPs when used in very small amount (5.4 mg for about 150 mg of SilAg batch). Besides the promising catalytic activity, as discussed above, the DVS data obtained were rather similar to Aerosil, which opens new opportunities for future work.

### 4. Conclusions

A silica-silver nanocomposite was prepared using AgNPs obtained with a glucose-containing cyclosiloxane as reducing agent and stabilizer, and TEOS in a modified sol-gel process. The resulting material was characterized by FTIR, AFM, SEM-EDX, TEM, XRD, XRF and DVS, and compared with silica models prepared in similar conditions. The water vapor sorption behavior, as well as the surface area and pore size calculated from DVS data were influenced by the presence of AgNPs in the silica framework and by the basic medium used for its preparation. The obtained silica-silver nanocomposite has potential applications in catalysis, as revealed by preliminary results on hydrogen peroxide decomposition.

### Table 2. Moisture sorption behavior and GAB analysis results for calcined samples and Aerosil.

| Sample | Weight gained (%) (“Prog1”) | The average pore size (radius, nm) | GAB_H₂O analysis (5-90%RH) | Weight gained (%) (“Prog2”) | Rₜ (% min⁻¹) | Weight loss (%) (“Prog2”) | Rₕ (% min⁻¹) |
|--------|----------------------------|-----------------------------------|---------------------------|----------------------------|---------------|----------------------------|---------------|
| SilAg  | 23.95                      | 2.3                               | 209.757                   | 0.0598                     | 32.36         | 0.35                       | 23.74         |
| Sil0   | 32.61                      | 5.9                               | 111.457                   | 0.0317                     | 41.03         | 0.24                       | 32.49         |
| Sil1   | 62.98                      | 8.1                               | 155.125                   | 0.0442                     | 69.14         | 0.52                       | 64.48         |
| Aerosil| 19.39                      | 3.5                               | 117.554                   | 0.0334                     | 31.37         | 0.19                       | 31.06         |

*All weight% are reported to the dry sample.*
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