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Silver nanoparticle growth in 3D-hexagonal mesoporous silica films

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The 3D-hexagonal mesoporous films are used as templates to grow uniform silver nanoparticles. The grafting of hydrophobic groups at the pore surface, significantly slows down the silver ion diffusion, anchoring small silver clusters in micropores and leading to organized domains of silver particles in mesopores with a narrow size distribution.

In the last years, mesoporous silica powders, such as the well-known MCM-41 ones, have been used as molds for the growth of different metallic nanoparticles, in order to control their size, shape and organization. For example, after impregnation of a ionic solution into mesoporous powders, gold and nickel spherical nanoparticles,[1,2] and gold and platinum nano-wires[3] have been synthesized by chemical or hydrogen reduction. Mesoporous silica films have also been used as templates to prepare uniform nanoparticles of gold and platinum.[4]

In contrast, the control of the growth of silver particles seems to be more difficult. A random distribution with large particles has generally been observed.[5–8] However, Wang *et al.* have obtained small organized domains in MCM-48, coexisting with large silver particles.[7] Besides, the control of the shape has been shown by Huang *et al.* and Han *et al.* who have synthesized silver nano-wires in SBA-15 powders.[5,6]

Recently, we have reported the synthesis of highly textured mesoporous silica films organized over the whole film thickness.[9] They have a 3D hexagonal structure of spherical mesopores, with the *c*-hexagonal axis oriented perpendicular to the film plane. Moreover, the open porosity of these films, probably *via* micropores located in silica walls, allows the impregnation by different solutions, which is necessary to fill the pores with nanoparticles. We report here the synthesis of silver nanoparticles inside these 3D hexagonal mesoporous silica films.

Mesoporous matrices were synthesized using a previously described procedure.[9] The polymeric silica sol was prepared by mixing TEOS ($Si(OC_2H_5)_4$), water (pH = 1.25) and ethanol in the 1 : 5 : 3.8 molar ratio, and aged 1 h at 60 °C. The well-known CTAB template was then added with the CTAB : TEOS molar ratio equal to 0.1. The obtained solution was diluted with ethanol (1 : 1) and spin-coated at 3000 rpm on Pyrex slides or pure silica substrates. The films were then calcined in air at 450 °C to remove the surfactant molecules. Silver ions were introduced by impregnation of films with a 0.1 M silver nitrate solution containing one molar equivalent of sodium citrate, completed with ammonia up to pH = 9.5. The film was then washed in deionized water and dried. After impregnation, Secondary Ion-Mass Spectrometry analyses (SIMS) showed an homogeneous distribution of silver ions as a function of the depth and Rutherford Backscattering Spectrometry (RBS) leads to a Ag/Si molar ratio of 0.08.

In a first experiment, the reduction of silver ions was performed by a Ar/H_2 gaseous mixture at 100 °C for 4 h. The UV-visible spectrum shows the characteristic plasmon peak at 415 nm corresponding to spherical silver particles (Fig. 1—curve a). The film was also studied by high resolution transmission electron microscopy (HRTEM) using a Topcon 002B microscope. The size distribution and the organization of the silver nanoparticles inside the film were studied by examining the film in cross section. Fig. 2a clearly indicates the presence of a random distribution of small silver particles and also of some particles larger than the pore size (about 4 nm). This leads to a large size distribution which broadens between 1 and 8 nm (average size of 3.2 nm and standard deviation of 1.33 nm). Therefore, concerning this experimental procedure, it is clear that the size of silver particles is not controlled by the pores of the mesoporous film. The presence of large particles, which damage the pore structure, is probably directly related to the fast diffusion of silver ions into the film. In fact, the reduction of these ions at the surface of a silver particle is thermodynamically enhanced, in comparison with the formation of new silver nuclei. On the one hand, in solution, the potential is more negative for the production of an isolated silver atom than for the reduction at the metallic bulk surface,[10] and on the other hand, the growth of silver particles is associated with the decrease of the surface energy. Therefore the ionic diffusion makes the growth of silver particles easier than their nucleation.

Assuming that the ionic silver diffusion in the mesoporous film takes place *via* the silanol groups, a second experimental procedure was performed in order to decrease the concentration of these groups at the pore surface. After impregnation, films were put under vacuum and treated by HMDS (hexamethyldisilazane) at 70 °C for 5 minutes. The resulting disappearance of silanol groups and the covalent grafting of $Si(CH_3)_3$ hydrophobic groups at the pore surface were checked by FTIR spectrometry (Si–OH band at 3740 cm^{-1}, C–H stretching bands at 2913 and 2954 cm^{-1} and C–H rocking band at 850 cm^{-1}). The reduction of silver ions was performed under the previous experimental conditions. Besides the plasmon peak at 415 nm,

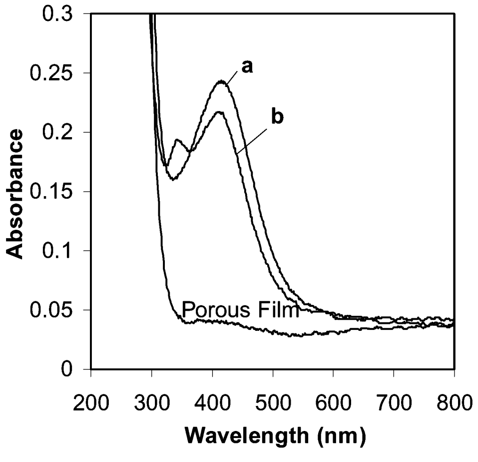

Fig. 1 UV-visible absorption spectrum of the film after reduction of silver ions (curve a). The curve b corresponds to the reduced film after a pretreatment by HMDS. The absorption below 350 nm is due to the Pyrex substrate.

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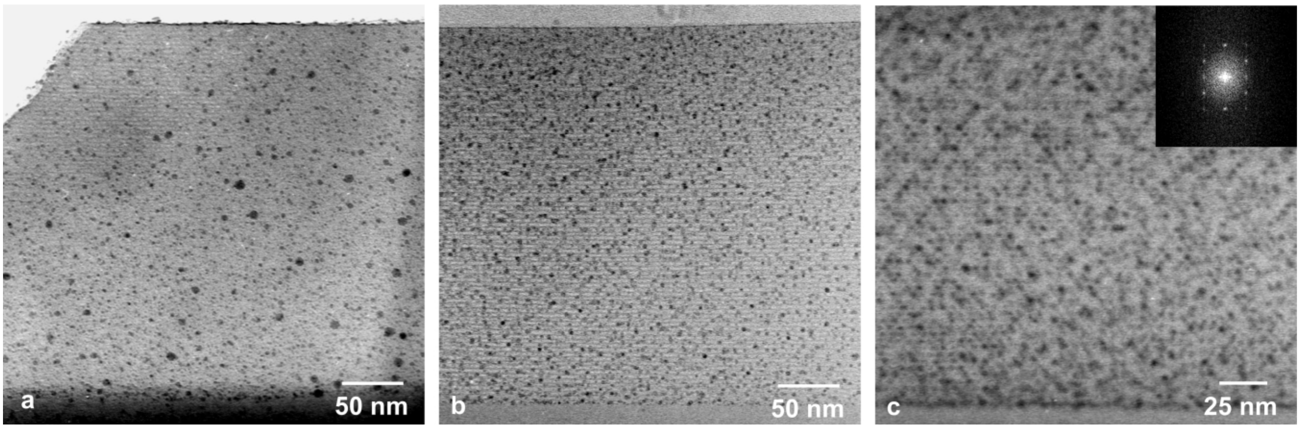

Fig. 2 HRTEM image of a cross section of the silver particles in mesoporous silica films. Silver ions are directly reduced after impregnation in an ionic solution (a). The impregnated film is treated by HMDS before reduction (b) and (c). The inset in (c) is the power spectrum of the image showing the 3D hexagonal structure.

the UV-visible spectrum, performed on a film pretreated by HMDS, exhibits small peaks at 345 (Fig. 1—curve b) and 310 nm. The last one is only observed for a film deposited on a pure silica substrate which is transparent above 250 nm. These peaks have been already observed for small silver clusters (from 2 to 8 atoms) synthesized in micropores of zeolites.[11] This suggests the stabilization of some silver clusters in the mesoporous films, probably located in microporous silica walls. Therefore, during the impregnation, silver ions are adsorbed both at the surface of mesopores and into silica walls.

The effect of the grafting by HMDS is clearly observed on the HRTEM cross-section (Fig. 2b). When compared with films prepared by the first procedure, there are no large particles and no segregation of particles near the substrate. The size distribution is narrow with an average size of 3.4 nm (standard deviation of 0.64 nm). However, the HRTEM image clearly shows that the filling ratio of the film is low. These results suggest that the ionic diffusion of silver ions is significantly reduced by the decrease of silanol groups but remains sufficiently important to enhance the growth of particles relative to the nucleus formation, leading to a random distribution of silver particles in films. Thus, an heterogeneous distribution of particles is still observed by using the procedure of successive cycles recently developed for CdS nanoparticles.[12] In this case, the film is hydrophobic after the first cycle due to the grafting by HMDS and ethanol is added to the solution (1 : 1 volume ratio) for the following impregnation. After four impregnation–reduction cycles, there is only a broadening of the size distribution (average size of 4 nm and standard deviation of 0.95 nm) and no significant change of the pore filling ratio. Nevertheless, after only one cycle, small organized domains of silver nanoparticles can be detected by HRTEM. Fig. 2c shows such a domain and its associated power spectrum in the inset. The latter was obtained by calculating the square modulus of the Fourier transform of the image. As previously shown,[12]there is an inversion of the image contrast giving rise to black dots over a white background when the mesoporous films are filled with nanoparticles. As a consequence, the Bragg peaks come from the periodicity of the array of nanoparticles and not from the mesoporous lattice. The power spectrum is characteristic of a view along the [2 1 1 0] zone axis of a 3D-hexagonal structure. The corresponding parameters are $a = 5.2$ nm and $c = 7.0$ nm, which are in agreement with the parameters of an empty mesoporous film.[9] Finally, the HRTEM image is a projection of the 3D structure and particles which are neighbors on the image can be located at a different depth into the film. However, this image perfectly indicates the formation of silver particles inside the periodic mesopores of the matrix although the filling is not complete.

To summarize, the major problem to obtain a periodic repetition of silver particles inside organized mesoporous films is related to the ability of silver ions to rapidly diffuse in an oxide network. This enhances the growth of large particles and prevents the rapid formation of nuclei in all the mesopores of the film. We have shown that the grafting of hydrophobic groups at the pore surface significantly slows down the ionic diffusion. This anchors small silver clusters in micropores and leads to small organized domains of particles in mesopores with a narrow size distribution. The complete filling of the film probably requires either to increase the concentration of silver ions after the impregnation or to use nuclei of another metal, with a lower ionic diffusion coefficient, for the growth of silver particles. Considering the first point, a solution is obviously to increase the starting silanol concentration in mesoporous films, which can be realized by changing the experimental procedure for the removal of the surfactant: washing in solvent instead of calcination. The second idea has also been exploited in SBA-15 powders, by Zhang *et al.*, to grow copper and nickel wires by electrolysis from a palladium starting nucleus.[13]

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