Ag nanoparticles synthesised in template-structured mesoporous silica films on a glass substrate

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Ag nanoparticles have been synthesised within a mesoporous template-structured silica film by a chemical route which includes ion-exchange with $Ag(NH_3)_2^+$ followed by reduction.

Thin films of surfactant-templated mesoporous metal oxides have been recently the focus of numerous studies.[1–6] In particular, a sol–gel-based dip-coating method for the rapid synthesis of continuous hexagonal and cubic mesoporous silica films has been developed.[3] The remarkable physico-chemical properties of these advanced materials (mesoporosity, unidimensional channels, preferable orientation with respect to the supporting substrate) are very promising for applications in membrane-based separation, catalysis and sensors. Here, we demonstrate a new potential of such films. Namely, we show that Ag nanoparticles can be chemically synthesised in the pores of mesoporous silica films deposited on glass substrates. To the best of our knowledge this development constitutes a novel application of mesoporous coatings which has, so far, not yet been described in the literature. However different applications of Ag nanoparticles have already initiated the development of numerous approaches for their elaboration, modification and incorporation into the surface layer of various materials *via* sol–gel processing,[7] melt-quenching,[8] electron beam lithography,[9] magnetron cosputtering,[10] ion-exchange,[11] ion-implantation,[12] or covalent linkage to self-assembled monolayers.[13]

Mesoporous silica films were synthesised using a precursor solution prepared in accordance with the published procedure[3] by addition of CTAB cationic surfactant [cetyltrimethylammonium bromide, $Me(CH_2)_{15}N^+Me_3Br^-$] to a silica sol with molar ratio 1 $Si(OC_2H_5)_4$: 22 C_2H_5OH : 5 H_2O : 0.004 HCl. The CTAB concentration in the final solution was 0.06 M, this reagent being essential for the formation of mesoporous silica films consisting of hexagonally packed one-dimensional channels adjacent to the air–film interface and shorter-range structural ordered channels in the core of the film.[3] The transparent and continuous films of *ca.* 100 nm thickness were deposited on Pyrex slides by dip-coating (10 cm min^{-1} withdrawal rate) at room temperature. Calcination in air at 400 °C (heating rate 1 °C min^{-1}) for 10 h resulted in films whose XRD patterns [Fig. 1(a) and (c)] are in accord with the formation of a mesophase with a $d(100)$ value of *ca.* 3.05 nm (assuming a hexagonal phase with a unit cell constant a = 3.52 nm).

For incorporation of silver, Pyrex slides covered with the calcined mesoporous silica films were contacted for 15 s with an aqueous solution of $[Ag(NH_3)_2]NO_3$ (prepared by dropwise addition of 28% $NH_3(aq)$ to 0.05 M aqueous $AgNO_3$ leading to the formation of a clear colourless solution), rinsed thoroughly with deionised water and dried in a stream of nitrogen at room temperature. For the reduction of silver, the as-synthesised samples were treated in an H_2–N_2 (5% H_2) flow at different temperatures (heating rate 5 °C min^{-1}) for 1 h.

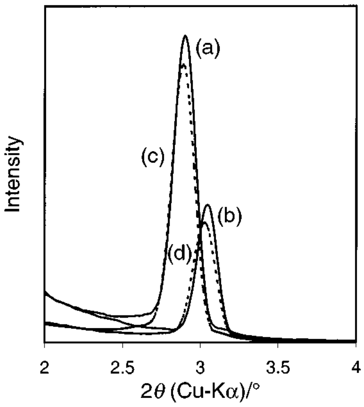

Fig. 1 XRD patterns of two Pyrex substrates with mesoporous silica films after calcination at 400 °C. Before/after [(a)/(b)] contact with an aqueous solution of $[Ag(NH_3)_2]$ NO_3 and subsequent reductive treatment at 400 °C. Before/after [(c)/(d)] contact with an ammoniacal solution and subsequent reductive treatment at 400 °C.

The presence of Ag^+ ions in the mesoporous film after contact with the solution of $[Ag(NH_3)_2]NO_3$ was detected by XPS. X-Ray photoelectron spectra of the as-synthesised samples reveal the presence of intense Ag $3d_{3/2}$ and Ag $3d_{5/2}$ peaks at 374.5 and 368.4 eV, respectively, characteristic for Ag^+.[14] It is reasonable to suggest the following ion-exchange mechanism of silver incorporation into the mesoporous film [eqn. (1)], as a consequence of deprotonation of hydroxy groups

$$Si–OH + Ag(NH_3)_2^+ = Si–OAg(NH_3)_2 + H^+ \qquad (1)$$

at the pore surface.[6] Assuming a uniform distribution of Ag^+ ions in the film, their concentration was estimated from the integral intensities of Ag 3d (374.5–368.4 eV) and Si 2p (103.8 eV) envelopes and the atomic sensitivity factors of Ag and Si.[14,15] The experimental I_{Ag}/I_{Si} ratio was close to 3.3 which corresponds to an Ag/Si atomic ratio of 0.17 or to *ca.* 10 wt.% of silver in the mesoporous silica film.

The as-synthesised samples were colourless [Fig. 2(a)] while a yellowish colour appeared after reductive treatment at 100 °C and the intensity of the absorption peak at *ca.* 410–435 nm progressively increased up to 500 °C [Fig. 2(b)–(f)]. The presence of this peak is consistent with the surface plasmon resonance of Ag nanoparticles[8] which are formed upon reduction. The position and the width of the plasmon resonance peak can give information about the average diameter of the nanoparticles. The observed blue shift of the plasmon resonance peak from 435 to 410 nm and the decrease of its width [Fig. 2(b)–(f)] can be related to the increase of the average particle diameter when the reductive treatment continues.[8]

In the X-ray photoelectron spectrum of the sample reduced at 400 °C, the I_{Ag}/I_{Si} ratio was 1.2. This decrease in comparison with the value observed in the as-synthesised sample indicates aggregation of the Ag atoms upon reductive treatment.[16] The formation of the Ag nanoparticles commences with reduction of

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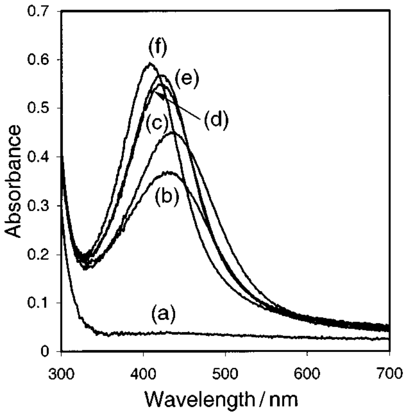

Fig. 2 UV–VIS spectra of a Pyrex slide covered with calcined mesoporous silica film after contacting with an aqueous solution of $[Ag(NH_3)_2]NO_3$ and drying in air (a), and subsequent reductive treatment at 100 °C (b), 200 °C (c), 300 °C (d), 400 °C (e) and 500 °C (f).

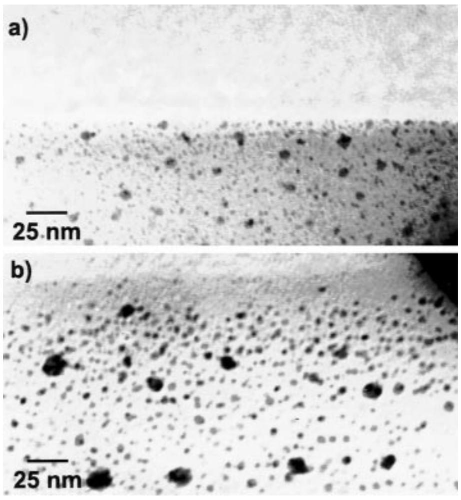

Fig. 3 Transmission electron micrographs of the calcined mesoporous silica film observed in cross-section view after one (a) and three (b) contacts with an aqueous solution of $[Ag(NH_3)_2]NO_3$ and subsequent reductive treatment at 400 °C.

Ag^+ to Ag^0 atoms which migrate within the silica mesoporous matrix.

The sample reduced at 400 °C was also characterised by transmission electron microscopy (TEM) [Fig. 3(a)]. Two types of Ag nanoparticles of different diameter can be distinguished. The first consists in nanoparticles of an almost spherical shape and of 3 nm average diameter while the second type is characterised by an average diameter of 6–7 nm. The existence of two sizes may be ascribed to the presence of defects, such as locally coalesced pores or walls. All particles are well separated from each other and are homogeneously and randomly distributed in the mesoporous silica matrix except in the vicinity of the external surface where ordering of Ag nanoparticles parallel to the surface is clearly seen. This ordering can reasonably be attributed to the preferable parallel orientation of the pore channels in the upper part of the film.[3] This supports the idea that the periodicity of the porous matrix can at least partially control the spatial arrangement of the nanoparticles.

As can be seen from Fig. 1(a) and (b), contact of the calcined sample with the $[Ag(NH_3)_2]NO_3$ solution followed by reductive treatment results in the partial shrinkage of the initial film (decrease of the 1-dH mesophase unit cell constant from *ca.* 3.52 to 3.35 nm). Also, a decrease of the peak intensity at constant width is observed which reveals a decrease of the volumic fraction of the ordered mesoporous domains. In order to ascertain if these effects are connected with the formation of Ag nanoparticles, a sample covered with the calcined film was treated according to the above procedure except that the ammoniacal solution did not contain $AgNO_3$ [Fig. 1(c) and (d)]. Comparing the positions and the relative intensities of the XRD peaks in Fig. 1 it can be concluded that similar modifications occurred for contact with both solutions. This means that both effects are connected with the chemical interaction of the mesoporous silica film with the ammoniacal solution rather than with the formation of Ag nanoparticles. Condensation of the silica framework promoted by ammonia has been reported previously.[4]

Since the organisation of the silica mesoporous film was maintained upon incorporation of Ag nanoparticles, it appeared possible to increase the silver concentration inside the pores. A progressive increase of the intensity of the surface plasmon resonance peak of Ag nanoparticles at 425 nm was indeed observed when the sample was successively contacted with $[Ag(NH_3)_2]NO_3$ solution and subjected to reductive treatment at 400 °C twice and three times.

The sample subjected to three consecutive ion-exchanges and reduction at 400 °C has been characterised by TEM [Fig. 3(b)]. As for the once only treated sample, two types of Ag nanoparticles are observed. Most are of almost spherical shape having an average diameter reaching 5 nm predominate while only a few larger Ag nanoparticles of an average diameter approaching 11 nm are present. The particles are well separated from each other and are homogeneously distributed in the mesoporous silica matrix. It appears that the particles diameter is not limited by the pore size.

In order to clarify whether the possibility of fabrication of Ag nanoparticles in mesoporous silica film relates to its unique structure, a silica film was dip-coated on a Pyrex substrate in the same manner from a precursor solution containing all reactants except CTAB. In this case of a non-mesoporous silica film no evidence of formation of Ag nanoparticles was observed.

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