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2006 J. Phys.: Condens. Matter 18 S85

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Organized mesoporous silica films as templates for the elaboration of organized nanoparticle networks

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Received 6 January 2006, in final form 1 March 2006

Published 13 March 2006

Online at stacks.iop.org/JPhysCM/18/S85

Abstract

Tremendous work achieved in the last 20 years on nanoparticle synthesis has allowed us to study many new physical properties that are found in the nanometre size range. New developments are now expected when considering assemblies of nanoparticles such as 2D or 3D organized arrays. These systems are indeed expected to exhibit original physical properties resulting from particle–particle interactions. Studies in this field are clearly dependent on the elaboration of materials with controlled particle size, organization and interparticle distance. This paper presents a strategy of elaboration that is based on the use of organized mesoporous silica films as templates. These films are made by sol–gel polymerization around surfactant assemblies and further elimination of the surfactant. This provides porous matrices with a pore organization that is the almost perfect replica of the initial micellar structure. The use of such films for the elaboration of organized arrays of nanoparticles is detailed in the case of CdS and Ag particles. The formation of particles inside the pores is achieved through impregnation with precursors that are allowed to diffuse inside the pores. This leads to particles with a size and a spatial arrangement that is directly related to the initial pore structure of the films. This process opens a wide range of investigations due to the relative ease of fabrication over large surfaces and the numerous possibilities offered by the elaboration of porous films with different pore sizes and organizations.

1. Introduction

It is now well known that the physical properties of materials may be drastically modified when considering small particles with a size in the nanometre range. A huge amount of work has been achieved in the last 30 years for the synthesis of nanoparticles with a tuneable size and a narrow size distribution. This has allowed a good physical description of many size

effects such as plasmon resonance in metal particles, quantum size effects in semiconductors and superparamagnetism in magnetic oxides or metals.

Now, new developments of research in the field of nanoparticles are expected when studying more complex systems in which the particles are associated with another compound having its own specific properties. Different kinds of heterostructure may be studied, the most representative being core/shell nanostructures or particles in interaction.

Concerning the properties that can be expected in such heterostructures, the simplest case is when they are only the addition of the properties of each component taken separately. The main interest then relies on the confinement of two different properties within the same nano-object, suitable for further manipulations depending on the applications. For example, magnetic particles have been associated with luminescent dyes [1] or luminescent semiconductor particles have been covered with a magnetic shell [2]. In other cases, a property of one of the components of the heterostructure is enhanced or optimized by the other one. A well known example is the case of highly luminescent CdSe/ZnS core/shell nanoparticles, in which the ZnS shell acts as a passivation layer against non-radiative relaxation from the emitting CdSe core particle [3].

Finally, the case that is probably the most interesting and opens a new field of investigation is when the properties of the heterostructure are drastically modified as compared with those of each component taken independently. This may be observed when there is a strong coupling between the different components of the heterostructure, i.e. when the characteristic length scales of the interactions are in the nanometre range. This is for example the case when considering energy transfer within luminescent systems such as between CdSe nanoparticles and surface grafted luminescent dyes [4], coupling between magnetic particles [5], or plasmon coupling between metallic particles [6]. A nice example on metallic particles is given by the work of Prikulis and co-workers [7], who studied the evolution of the scattering spectra of two silver nanoparticles that are brought together using an optical tweezer experimental set-up. The strong coupling of the plasmon resonance between the two particles in close contact leads to a spectacular change of the colour of the scattered light.

The next step in this field of research is to study the interactions that may occur not only between two particles, but between a large numbers of particles. Provided that the interactions are sufficient, collective effects may now take place due to interactions resulting from the coupling between a large numbers of particles, and leading to spectacular physical properties of the assembly of particles [5, 6, 8]. Since these interactions are strongly dependent on the distance between the particles, it clearly appears that any careful study and optimization of collective effects in nanoparticle assemblies require the elaboration of ordered networks. As at the beginning of research on the properties of nanoparticles, when the synthesis of well controlled particles was the limiting step for the investigation of size effects, it is clear that the precise study of collective effects first requires to answer the problem of the elaboration of materials.

2. General strategies toward ordered arrays of nanoparticles

A first approach for the elaboration of periodic networks of nanoparticles consists in using lithography, so that the size, shape and organization of the particles may be controlled as desired. Using electron beam lithography, Felidj and co-workers were able to produce various arrays of gold particles with a size of about 60 nm and a particle distance of a few hundred nanometres (figure 1) [9]. Although nice results could be obtained on the optical properties of these systems, the limited resolution of lithographic techniques does not allow us to decrease the interparticle distances much less than about a hundred nanometres.

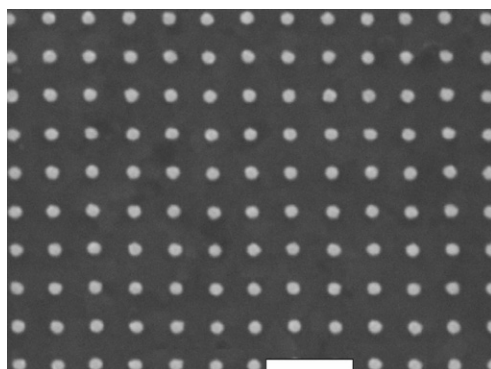


Figure 1. SEM image of a gold nanoparticle network, obtained using electron beam lithography, the scalebar corresponds to 700 nm (adapted from Felidj and co-workers).

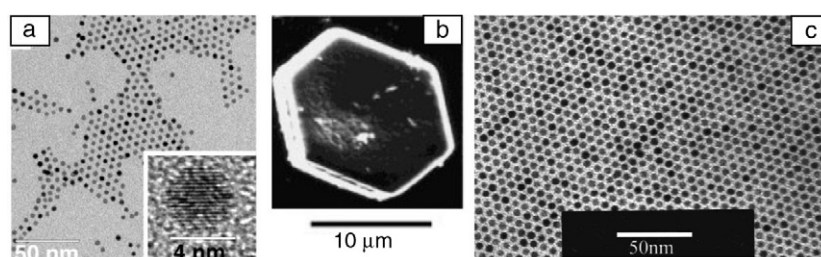


Figure 2. Spontaneous self-organization of colloidal CoPt_3 nanoparticles into a 2D network (a) and macroscopic crystal obtained by 3D organization of the same particles (b) (adapted from Shevchenko and co-workers [12]). (c) Long range ordered 2D array of gold particles deposited on a Si_3N_4 wafer (adapted from Lin and co-workers [13]).

The other approach is to use the property of colloidal nanoparticles to assemble themselves directly into periodic arrays, though a process known as self-organization, which is similar to crystallization. Well known examples of such spontaneous arrangements are colloidal crystals [10] obtained from highly charged latex particles in solution, and artificial opals made through the slow decantation of silica particles [11]. In both cases, the important factors allowing self-organization of the particles is their high monodispersity and their high stability in the dispersion media. Recent developments of colloid chemistry have allowed the synthesis of particles with a very good control of their size, which are usually surface functionalized with long alkyl chains so that they can be stabilized in organic solvent with high concentration [12]. It has been shown in many examples that the slow evaporation of the solvent leads to spontaneous formation of crystals of particles either 2D (figure 2(a)) [13] or 3D (figure 2(b)) [14, 15]. The main problem is that the dimensions of the organized domains are usually small (less than a few hundred nanometres). As for classical crystal growth, improvement may nevertheless be obtained through the careful control of nucleation/growth of the structure, which can be optimized to some extent by altering the experimental conditions, and especially the evaporation rate of the solvent and the surface functionalization of the substrate. As in the work reported by Lin and co-workers [13] on gold particles, it is then possible to obtain 2D structures with an almost perfect organization over several microns.

The latter method of elaboration of organized arrays of particles through self-assembly from colloidal suspension is limited to a few compounds in which synthesis has been optimized

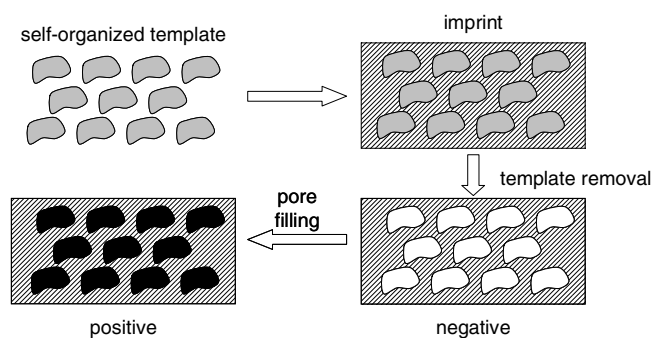


Figure 3. General principle of the template approach for the elaboration of an organized network of particles (see text).

to have narrow size distribution and an appropriate surface state. The template strategy tries to overcome these limitations by starting from systems that are known to spontaneously self-organize quite easily, and use them as templates or moulds to transfer their organization for the compound of interest. The general process is briefly given in figure 3.

A self-organized system is infiltrated by a matrix and further removed by dissolution or calcination. This provides a mould into which the precursors of the compound of interest are infiltrated, leading to the replica of the initial organization. Many different systems have been used. They usually consist in colloidal species that can be synthesized quite easily as very monodisperse particles such as Stöber silica or latex particles [16], or that are provided naturally like viruses or proteins such as ferritin [17]. In other cases, such as porous aluminium membranes, a specific process of elaboration provides ordered arrays of monodisperse pores that can be used directly as templates for the elaboration of nanowires [18]. In the following section, the template approach will be described in detail in the case of micellar structures obtained using surfactant molecules that spontaneously self-assemble in solution into many different structures. These structures can be used as templates for the elaboration of organized pore networks within a silica matrix, providing a new and versatile template for the elaboration of organized networks of particles;

3. Organized mesoporous thin films as templates

3.1. Sol-gel synthesis of organized mesoporous materials

Sol-gel chemistry is now a well known method for the elaboration of materials through ‘soft chemistry’ routes. Its basic principle relies on the controlled polymerization or precipitation of inorganic materials from molecular precursors in solution [19]. Although many oxide compounds have been synthesized, silica remains one of the most important, mostly because the chemical properties of silicon allow a remarkable control of polymerization processes. Moreover, a large number of silicon precursors is known, and the stability of the Si-C chemical bonds opens up the way towards inorganic/organic materials.

Sol-gel synthesis of silica is usually achieved from alkoxides through hydrolysis/condensation reactions of polymerization. The structure of the obtained solid depends strongly on the pH of the water used for hydrolysis, which governs the relative kinetics of hydrolysis and condensation reactions. Basic media allow the synthesis of remarkable silica particles such as described in the famous Stöber process [20], while acid hydrolysis leads to homogeneous polymerization, which allows the synthesis of transparent materials following

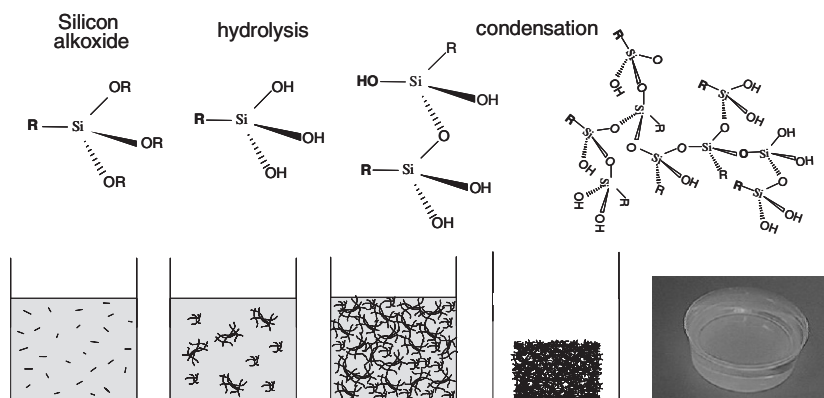


Figure 4. Schematic description of the sol-gel synthesis of transparent silica matrices.

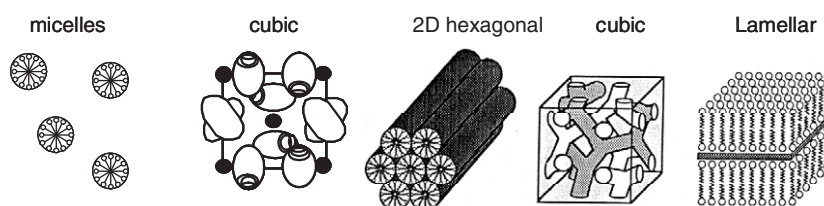


Figure 5. Structures that are classically observed in many surfactant/water/oil phase diagrams with a low concentration of oil and an increasing concentration of surfactant from left to right.

the well known sol-gel process as described in figure 4. As they are synthesized at low temperature, these latter materials have found numerous applications as host matrices for many organic molecules, in particular dyes with specific optical properties [21].

Since about 10 years ago, and starting with the pioneering work of Kresger and his coworkers [22], a new field of applications concerns the association of sol-gel chemistry and surfactant assemblies. It has been known for a long time that surfactant molecules self-assemble in the presence of water and oil (usually a hydrocarbon) to form different structures depending on the composition in a ternary phase diagram. Some of these structures present a remarkably high degree of organization (figure 5).

The idea is then to stabilize surfactant assemblies by achieving the sol-gel polymerization of an inorganic compound around the micelles. After complete drying of the material, the surfactant may be withdrawn (for example by calcination at 450 °C) so that the final material presents a porosity which is a replica of the initial surfactant structure.

Organized mesoporous materials are then characterized by a porous structure as described in figure 6, and present the following general characteristics.

- There are two kinds of pore: micropores and mesopores.
- Micropores are located within the oxide walls between the mesopores. They result from the incomplete condensation of the oxide precursor. Their dimensions are typically of a few ångströms.
- Mesopores are the negative structure of the micellar organization existing just after the synthesis of the material.
- The dimensions of the mesopores are typically in the 3–10 nm range. They may represent more than 30% of the total volume of the material.

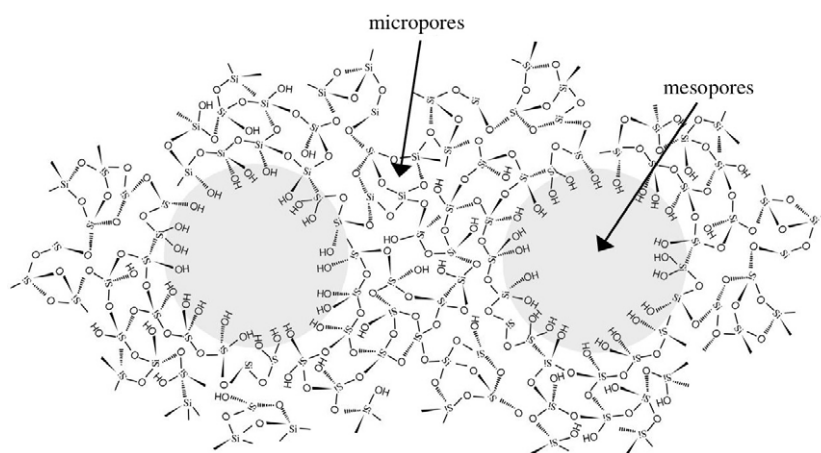


Figure 6. Schematic representation of the pores structures in organized mesoporous silica materials.

- The mesopores are monodisperse and organized through a periodic network, with a textured structure which depends on the experimental conditions used for the synthesis of the material and the nature of the surfactant which has been used.

The original structure of organized mesoporous material is at the basis of a huge number of works in the last ten years, motivated by numerous applications, most of which aim to take advantage of the very high surface area of the materials and the original structure of the pores. Material processing may be achieved to use the properties of the materials in many different forms such as powders, fibres, thin films or monoliths [23].

Thin films of organized mesoporous silica may find numerous applications for the surface functionalization of various substrates (glass, fibres, plastics, semiconductors ...). A first class of applications concerns the use of the very high specific surface of the mesoporous films. This allows the chemical grafting with a very high density of species with a specific activity (catalysis, stain, hydrophobic coating ...). A second class of applications concerns the property of porous coating to have very low dielectric constant and refractive indices. Finally, ordered mesoporous films may be used as templates for the elaboration of periodic networks of particles which are grown inside each pore. In this case, it allows more fundamental research on collective effects in the physical properties of periodically assembled nanoparticles of metals, semiconductor or magnetic materials.

3.2. Organized mesoporous silica thin films

The elaboration of mesoporous silica films has been the subject of many investigations, mainly using spin or dip-coating methods of deposition [24, 25]. In a typical procedure, a silica sol is prepared by acidic hydrolysis of tetraethoxysilane (TEOS) in ethanol, and further ageing to achieve a partial condensation to form silica aggregates. The surfactant is added into this sol just before its deposition, with a concentration corresponding to a given surfactant/silicon molar ratio. The obtained solution is deposited on the substrate, for example by spin or dip coating. During the deposition process, the ethanol evaporates so that the volume fractions of both the surfactant and the silica aggregates increase. As the silica phase is polar and contains water, micellar aggregation of the surfactant occurs, followed by self-assembly of the micelles. As evaporation goes on, the structure evolves due to the increase of the surfactant volume fraction, until the moment when the structure is fixed by the sol-gel transition of the percolating silica

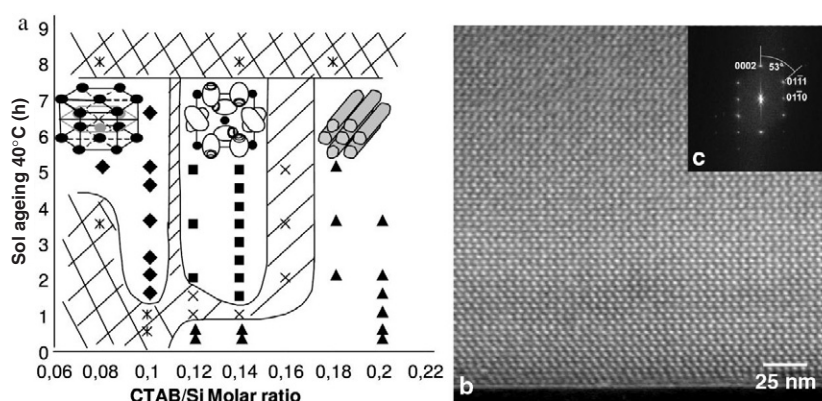


Figure 7. (a) Diagram of the phases obtained using CTAB as a surfactant template (diamond, 3D hexagonal; squares, cubic; triangles, 2D hexagonal) [26]. (b) Cross section view by electron microscopy of a film with the 3D hexagonal pore structure; (inset (c)) power spectrum of the same picture.

aggregates. After complete drying of the film at moderate temperature, the surfactant may be withdrawn by calcination at typically 450 °C.

Structural characterization of the porous structure may be achieved by using x-ray diffraction, glancing incidence small angle x-ray scattering, and electron microscopy. In the particular case when the surfactant used is the classic CTAB (cetyltrimethylammonium bromide), it is found that the structure of the films strongly depends on the surfactant/silica molar ratio, and the time for which the silica sol has been aged before deposition. A diagram of the different phases obtained was established, showing unsurprisingly that the structure depends on the relative volume fraction of the surfactant and the silica phase (figure 7(a)) [26]. This relative volume fraction depends on the surfactant/silicon molar ratio, and on the size of the silica aggregates, which determines the volume fraction of the polar phase at the moment of their percolation. The vapour pressure in the environment of the films during the deposition and drying steps was also found to be a parameter determining the quality of the structure, probably since it determines the amount of water in the film at the sol–gel transition and so the volume fraction of the polar phase [27].

Three different structures were obtained: the cubic and the hexagonal were classically observed in thermodynamically stable surfactant assemblies in solution, but the 3D hexagonal appears to be almost original, and its formation directly related to the stabilization of a transient association of micelles. In all cases, the structures are textured. For example, the *c*-axis of the 3D hexagonal phase is always perpendicular to the surface of the substrate. The structure of the film is almost perfect for thickness less than around 400 nm, and in plane domains extend for a few hundred nanometres (figure 7(b)).

The same method of elaboration may be achieved with other surfactant templates, among which are block copolymers such as PPO–PEO–PPO (PPO = polypropylene oxide, PEO = polyethylene oxide). As an example, perfectly organized films with an orthorhombic pore structure were obtained using pluronic PE6800 (figure 8) [28].

3.3. Application of organized mesoporous thin films as templates for the elaboration of 3D arrays of nanoparticles

The structure of mesoporous thin films makes them good candidates for being used as templates for the elaboration of an organized network of nanoparticles. Their process of elaboration may

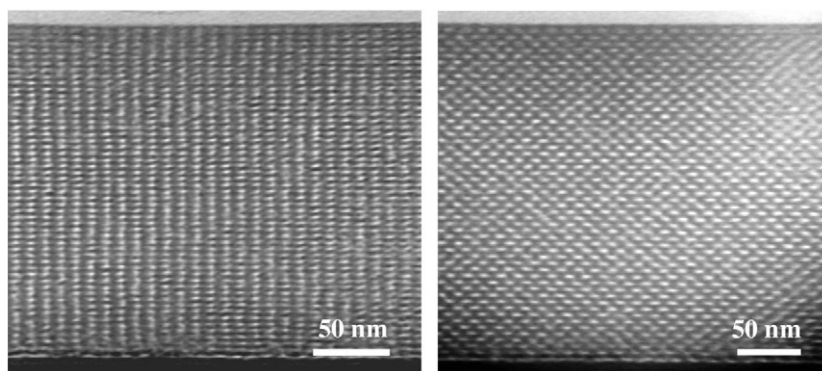


Figure 8. Transmission electron microscopy image of a film made with the triblock PPO-PEO-PPO PE6800 copolymer. Transverse section views as seen on two different directions.

be achieved quite easily over large surfaces. Moreover, their structures and pore sizes and shapes may be varied by altering the different parameters of their synthesis.

The basic principle is then to achieve the precipitation of nanoparticles in the mesopores through impregnation of the films with precursors that are allowed to diffuse over all the film thickness thanks to both micro- and mesopores. The precipitation process has to be optimized so that each pore is finally filled with one particle, within the whole film thickness.

3.3.1. 3D arrays of CdS nanoparticles. CdS nanoparticles have been widely investigated, and their optical properties are well understood in terms of quantum confinement [29]. Size effects are clearly visible considering the absorption spectra of the particles for which the absorption threshold changes from 530 nm for particles of diameter greater than 8 nm down to 350 nm for 1 nm particles [30].

Precipitation of CdS within the pores of the films may be achieved in a three-step process [31]: (a) impregnation of the film with a solution of Cd^{2+} ions, the pH of which was optimized to ensure their complexation by the silanol groups; (b) washing of the film to remove any excess Cd^{2+} ions; and (c) precipitation of the CdS particles by rapid injection of H_2S into the vessel containing the films. This cycle is repeated until saturation of the film as monitored by its absorbance spectra.

After each cycle, the film is studied by x-ray diffraction (figure 9, left). The main peak is characteristic of the periodic porous structure [24]. Its intensity strongly decreases during the first cycle, and then slowly increases again. This is attributed to an inversion of the electronic contrast of diffraction, due to the fact that the pores are progressively replaced by CdS, which has a higher electron density than the sol-gel silica walls around the pores. The evolution of the absorbance spectra of the same film (figure 9, right) clearly shows the typical spectra from quantum confined CdS particles. The absorption onset shifts to the red after each cycle of impregnation, which attests to the growth of the particle. The particle size may be determined using well established size/gap correlation [30], which shows that saturation is observed when the particles have a diameter of about 3.5 nm. This size corresponds well with the dimension of the mesopores in the empty film. Transmission electron microscopy imaging of the empty and filled films in transverse section confirms that each pore is filled with a CdS particle of roughly the same size (figure 10). The same effect of contrast inversion is observed as for x-ray scattering experiments, since for a given defocalization of the microscope the CdS particles appear as black dots (figure 10, right), while empty pores correspond to white dots (figure 10,

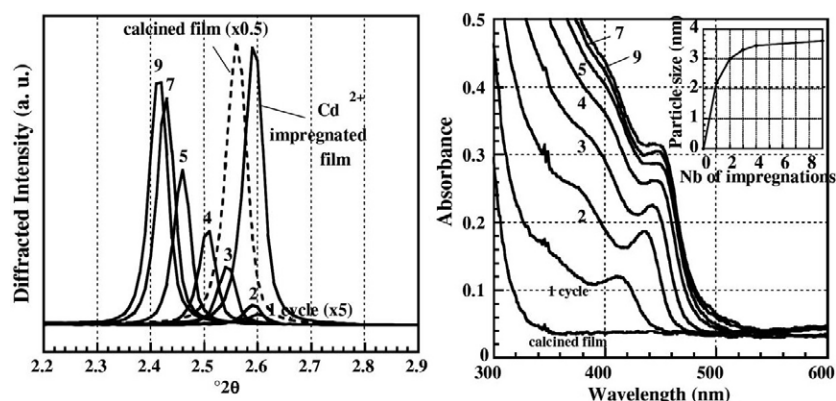


Figure 9. Evolution of the x-ray diffraction diagram (left) and absorbance spectra (right) of a mesoporous film after each cycle of CdS precipitation. Inset: evolution of the size of the particles as deduced from their onset of absorption. Adapted from [31].

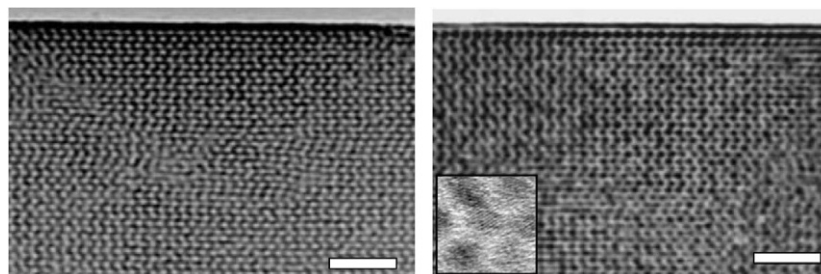


Figure 10. Transmission electron microscopy images (transverse sections) of an empty (left) and a CdS filled film. The scale bar corresponds to 30 nm. Inset: high resolution image of a few particles.

left). Note that the contrast of the CdS particles comes both from their electronic density and their diffraction.

3.3.2. 3D array of metal nanoparticles. The same process as for CdS nanoparticles was adapted for gold and silver. Reduction of the Ag^+ was achieved by thermal treatment of the films at 100°C under a dilute atmosphere of hydrogen [32]. First results clearly showed that the nanoparticles were localized anywhere in the film without any relation with the mesoporous structure (figure 11(a)). Moreover, their size distribution is broad, and no saturation could be observed (i.e. absorbance of the film continuously grown after all impregnation cycle). This problem is attributed to a high mobility of the silver ions within the film, and the difficulty of having one silver particle nucleating in each pore. In fact, it is the basic principle of photography [33] that the reduction potential of silver ions at the surface of existing particles ($E^\circ[\text{Ag}^+/\text{Ag}_{\text{bulk}}] = +0.8 \text{ V/NHE}$) is much more favourable than the reduction of silver ions to silver atoms or very small silver germs ($E^\circ[\text{Ag}^+/\text{Ag}_0] = -1.8 \text{ V/NHE}$).

Improvement of the material could be obtained by decreasing the mobility of the silver ions in order to limit the growth rate of the particles. Diffusion of Ag^+ ions occurs mainly through the silanol groups located at the surface and inside the silica walls around the mesopores. Grafting of trimethylsilyl groups ($\text{Si-OH} \mapsto \text{Si-O-Si}(\text{CH}_3)_3$) was achieved just after the first impregnation with the silver ions in order to both reduce the number of silanols and create

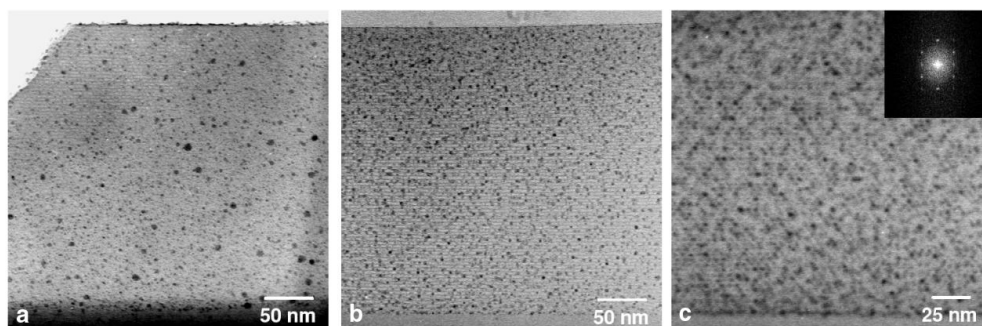


Figure 11. Transmission electron microscopy image of a mesoporous film with Ag nanoparticles. Without HMDS treatment (a), with HMDS treatment ((b), (c)). Inset of (c): power spectrum of (c).

a hydrophobic barrier between the mesopores. Such a grafting is easily made by just having the films in the presence of hexamethyldisilazane vapours [32]. After this treatment, the size distribution of the Ag particles appears much narrower than in the untreated films and almost all particles are clearly located on the initial mesopores (figure 11(c)). Meanwhile, not all the pores are filled with silver particles after the first reduction process, and further impregnation steps (still possible using hydro-alcoholic solutions because the film is hydrophobic) only lead to the growth of already existing particles. Improvement must then be found for this process, especially in order to increase the silver loading in the film after the first impregnation.

4. Conclusion

New trends in the field of nanoparticle research concern the study of organized networks of nanoparticles, with the aim to study collective effects resulting from inter-particle interactions. These studies are highly dependent on processes of elaboration of materials with a well controlled structure and a high coherence length. Nice results may be obtained using direct self-assembly of colloidal nanoparticles. Nevertheless, this approach can only be applied to systems whose colloidal synthesis is very well controlled. Moreover, the coherence length of these organized structures is often limited to a few hundred nanometres.

The template method aims to provide a versatile approach by using well known self-assembling systems whose organization can be further transferred to the compounds of interest. An example of this strategy is given in the case of organized mesoporous silica films. These films are obtained by sol-gel polymerization of a silica precursor around micellar assemblies of a surfactant. Further elimination of the surfactant by calcination leaves a pore network that is an almost perfect replica of the initial micellar structure. The pore size and organization may be varied by altering the experimental conditions, and the films are structured over all their thickness (typically 400 nm). Results are given concerning the precipitation of CdS and Ag particles inside the pores of the structure, showing the large possibilities offered by using these films for the production of organized networks of nanoparticles.

References

- [1] Lu Y, Yin Y, Mayers B T and Xia Y 2002 *Nano Lett.* **2** 183–6
- [2] Kim H, Achermann M, Balet L P, Hollingsworth J A and Klimov V I 2005 *J. Am. Chem. Soc.* **127** 544–6
- [3] Dabbousi B O, Rodriguez-Viejo J, Mikulec F V, Heine J R, Mattoussi H, Ober R, Jensen K F and Bawendi M G 1997 *J. Phys. Chem. B* **101** 9463

- [4] Clapp A R, Medintz I L, Mauro J M, Fisher B R, Bawendi M G and Mattoussi H 2004 *J. Am. Chem. Soc.* **126** 301–10
- [5] Dormann J L, Cherkaoui R, Spinu L, Nogues M, Lucari F, D’Orazio F, Fiorani D, Garcia A, Tronc E and Jolivet J P 1998 *J. Magn. Magn. Mater.* **187** L139–44
- [6] Ung T, Liz-Marzan L M and Mulvaney P 2001 *J. Phys. Chem. B* **105** 3441
- [7] Prikulis J, Svedberg F, Kall M, Enger J, Ramser K, Goksor M and Hanstorp D 2004 *Nano Lett.* **4** 115
- [8] Lazarides A A and Schatz G C 2000 *J. Phys. Chem.* **104** 460
- [9] Felidj N, Aubard J, Lévy G, Krenn J R, Salerno M, Schider G, Lamprecht B, Leitner A and Aussenegg F R 2002 *Phys. Rev. B* **65** 75419
- [10] Pieranski P 1984 *Contemp. Phys.* **24** 25
- [11] Mayoral R, Requena J, Moya J S, Lopez C, Cintas A, Miguez H, Meseguer F, Vazquez L, Holgado M and Blanco A 1997 *Adv. Mater.* **9** 257
- [12] Shevchenko E V, Talapin D V, Rogach A L, Kornowski A, Haase M and Weller H 2002 *J. Am. Chem. Soc.* **124** 11480–5
- [13] Lin X M, Jaeger H M, Sorensen C M and Klabunde K J 2001 *J. Phys. Chem. B* **105** 3353–7
- [14] Murray C B, Kagan C R and Bawendi M G 2000 *Annu. Rev. Mater. Sci.* **30** 545–610
- [15] Harfenist S A, Wang Z L, Whetten R L, Vezmar I and Alvarez M M 1997 *Adv. Mater.* **9** 817
- [16] Miguez H, Meseguer F, Lopez C, Lopez-Tejiera F and Sanchez-Dehesa J 2001 *Adv. Mater.* **13** 393–6
- [17] Yamashita I 2001 *Thin Solid Films* **393** 12–8
- [18] Rahman S and Yang H 2003 *Nano Lett.* **3** 439–42
- [19] Sanchez C, Henry M and Livage J 1998 *Prog. Solid State Chem.* **18** 259–341
- [20] Stober W, Fink A and Bohn E 1968 *J. Colloid Interface Sci.* **26** 62
- [21] Sanchez C, Lebeau B, Chaput F and Boilot J P 2003 *Adv. Mater.* **15** 1969–94
- [22] Kresge C T, Leonowicz M E, Roth W J, Vartuli J C and Beck J S 1992 *Nature* **359** 710–2
- [23] Barton T J, Bull L M, Klemperer W G, Loy D A, McEnaney B, Misono M, Monson P A, Pez G, Scherer G W, Vartuli J C and Yaghi O M 1999 *Chem. Mater.* **11** 2633–56
- [24] Besson S, Ricolleau C, Gacoin T, Jacquiod C and Boilot J P 2000 *J. Phys. Chem. B* **104** 12095–7
- [25] Grosso D, Babonneau F, Albouy P A, Amenitsch H, Balkenende A R, Brunet-Bruneau A and Rivory J 2002 *Chem. Mater.* **14** 931–9
- [26] Besson S, Gacoin T, Ricolleau C, Jacquiod C and Boilot J P 2003 *J. Mater. Chem.* **13** 404–9
- [27] Cagnol F, Grosso D, Soler-Illia G J D A S, Crepaldi E L, Babonneau F, Amenitsch H and Sanchez C 2003 *J. Mater. Chem.* **13** 61–6
- [28] Besson S, Ricolleau C, Gacoin T, Jacquiod C and Boilot J P 2003 *Micropor. Mesopor. Mater.* **60** 43–9
- [29] Eychmüller A 2000 *J. Phys. Chem. B* **104** 6514–28
- [30] Wang Y and Herron N 1990 *Phys. Rev. B* **42** 7253–5
- [31] Besson S, Gacoin T, Ricolleau C, Jacquiod C and Boilot J P 2002 *Nano Lett.* **2** 409–14
- [32] Besson S, Gacoin T, Ricolleau C and Boilot J P 2003 *Chem. Commun.* **3** 360–1
- [33] Belloni J, Mostafavi M, Marignier J L and Amblard J 1991 *J. Imaging Sci.* **35** 68–74