

# Nanostructured Metals Synthesized in Highly Swollen Liquid Crystals

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## ABSTRACT

We have developed a flexible approach for the preparation of nanostructured materials using swollen liquid crystals (SLCs) that exhibit hexagonal, cubic or lamellar symmetry as soft templates. The versatility of these structures as well as the extended domains of stability and the large range of accessible characteristic sizes make hexagonal SLCs perfect candidates for their use as matrixes for the synthesis and the confinement of nanomaterials. The final shape of the obtained nanostructures is deeply influenced by the morphology of the liquid crystal itself and it is possible to obtain nano-materials of various morphologies. SLCs can also be used as soft templates to organize self-assembly of nanoparticles into controlled shapes of larger characteristic sizes. We report the synthesis and characterization of platinum and palladium based nanofibers, nanowires, nanotubes or lamellae obtained in these mesophases.

**Keywords:** nanostructures, soft templates, self assembly, platinum, palladium, liquid crystals

## 1 INTRODUCTION

A lot of attention is currently focussed on well defined nanostructured materials because of their unique properties, and potential technological applications in semiconductors, metal catalysts and magnetic recording.<sup>1</sup> Thus, a large number of studies have been devoted to accurate control of the size and shape of nanoparticles. Many studies are based on point-initiated uniaxial growth of the crystal or the polymer. Porous hard templates have been widely used to obtain nanowires.<sup>2-6</sup> These hard templates are effective to obtain nanowires but they are not easy to remove, their dissolution in corrosive media being required to isolate the nanowires.

We have developed a flexible approach for the preparation of nanostructured materials in swollen liquid crystals (SLCs) as soft templates.<sup>7, 8</sup> This paper reports the synthesis and characterization of metallic and bimetallic nanofibers, tubes or lamellae obtained in these mesophases. The existence of hexagonal SLCs was first demonstrated by L. Ramos *et al.* in the phase diagram of quaternary mixtures containing the anionic surfactant (sodium dodecylsulfate: SDS), pentanol as co-surfactant, water and cyclohexane as

swelling phase.<sup>9,10</sup> The specificity of this system is based on the fact that the system still exhibits an oil in water (o/w) direct phase structure made of hexagonally packed nonpolar cylinders filled by cyclohexane, stabilized by a monolayer of the anionic surfactant (and co-surfactant) surrounded by a continuous water domain, even if the amount of oil is twice that of water. Earlier studies<sup>8</sup> have shown that the diameter of the nonpolar cylinders,  $R$  (Figure 1) can be monitored over a size range (from 3 to 30 nm) by adjusting the amount of cyclohexane ( $w$ ) and the ionic force of the aqueous solution, the distance between the adjacent cylinders being nearly constant (3 nm). The ionic force is adjusted by addition of salts such as sodium chloride. Magnetic particles of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> or metal nanoparticles could be inserted into the cyclohexane cylinders.<sup>11, 12</sup>

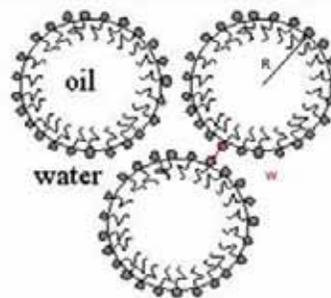


Figure 1. Cross section of a swollen hexagonal phase

## EXPERIMENTAL

The preparation of different samples of SLC was performed according to a general procedure starting with the dissolution of the surfactant (SDS, CTAB or CpCl) and salt into the aqueous phase and the addition of the organic swelling agent under mechanical stirring. The cosurfactant (pentanol) was added dropwise under energetic stirring with a vortex tube shaker. The hexagonal symmetry of this SLC was checked by small-angle X-ray scattering (SAXS) and optical microscopy. These SLCs can be doped with metallic or a mixture of metallic precursors (H<sub>2</sub>PtCl<sub>6</sub>, K<sub>2</sub>PtCl<sub>6</sub>, K<sub>2</sub>PtCl<sub>4</sub>, Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>, PdCl<sub>2</sub>, SnCl<sub>2</sub>, CoSO<sub>4</sub>,) which replace the sodium chloride of the original phases. These salts act also as additive for tuning the ionic force of the aqueous

phase. The resulting phases are translucent and birefringent, and exhibit the characteristic textures of hexagonal liquid crystal when viewed in polarized light microscopy. The SAXS experiments were performed using both synchrotron radiation and the laboratory setup. The doped hexagonal phases were reduced by gamma irradiation (using a  $^{60}\text{Co}$  gamma source, dose rate of  $5300 \text{ Gy}\cdot\text{h}^{-1}$ ), UV light or by chemical reduction techniques.

## RESULTS AND DISCUSSION

The structural properties of the system were probed by Small Angle X-ray Scattering (SAXS) experiments. The stability of these liquid crystals has been investigated when the pH of the aqueous medium or the chemical nature of the components (salt and surfactant) is changed. We demonstrated that the range of stability is quite extended, rendering swollen hexagonal phases potentially useful for the fabrication of nanomaterials.<sup>8,9</sup> This opens the way to the use of these highly swollen liquid crystals as nanoreacting media.

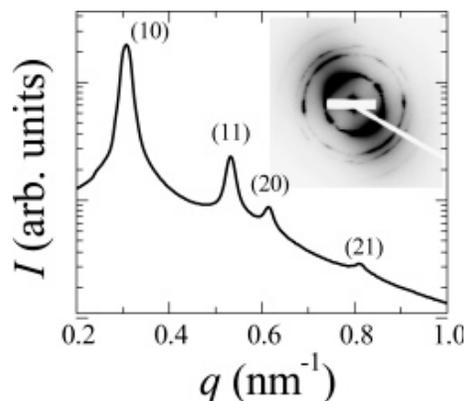
### 1. Stability of SDS based hexagonal phases

The starting point of this study is the swollen hexagonal phases comprising SDS as surfactant and different salts (NaCl, NaF, KCl,  $\text{Na}_2\text{SO}_4$  or metal salts). The structural parameters of the samples are determined on the basis of their SAXS patterns. Two or three Bragg peaks whose positions are in the ratio  $1:\sqrt{3}:2$  are usually observed for data obtained using the laboratory setup, and up to four peaks whose positions are in the ratio  $1:\sqrt{3}:2:\sqrt{7}$  are observed when synchrotron radiation is used. Our results suggest that swollen hexagonal phases may be obtained with a large variety of salts, used as pure components or as mixtures.<sup>8</sup> We have also investigated the stability of the SDS based hexagonal phases with acido-basic conditions. The swollen liquid crystals are stable over large range of pH (from pH 2 – 11). However at pH 1, the hexagonal phase structure was found to degrade within a few days (sealed samples of SLCs are usually stable for years). We assign this destructure to the progressive protonation of the sulfate head of the SDS surfactant, which precludes the long-term stabilization of SDS-based samples at lower pH.

As an example, the SAXS spectra of the doped phases with concentration of platinum  $[\text{H}_2\text{PtCl}_6] = 0.2 \text{ M}$  in the aqueous phase, are shown in Figure 2. Remarkably, we find that even at high salt concentration (upto 0.4 M for  $\text{H}_2\text{PtCl}_6$  and upto 0.1 M for Palladium and Cobalt salts) the  $P6mm$  hexagonal symmetry is preserved, with lattice parameters equal to that of the original hexagonal SLC obtained with NaCl as salt. Hence, the controlled addition of metallic salts in the aqueous phase did not disrupt the liquid crystalline phases. We have taken advantage of the remarkable possibilities offered by swollen hexagonal phases as nanoreacting media and have exploited these

SLCs to design anisotropic polymeric, inorganic, and metallic materials.<sup>7</sup>

### 2. Metal nanomaterials synthesized in SDS based hexagonal phases



**Figure 2.** SAXS spectrum and image plate recorded on the synchrotron beamline of a SLC made with SDS as surfactant and  $\text{H}_2\text{PtCl}_6$  as salt. The salt concentration is  $0.2 \text{ mol L}^{-1}$ , and the swelling ratio is  $\rho = 2$ ,  $\rho$  is the volume ratio of oil over water.

The SDS-cyclohexane-water direct hexagonal liquid crystal doped with metallic salts was used as a nanoreactor to synthesize metal nanomaterials. In our study, metal nanostructures were synthesized inside the aqueous phase of a SLC.

When a high irradiation dose of  $\gamma$  rays was applied (92 kGy with a SLC containing a 0.1 M aqueous solution of platinum acid), a complete amorphization of the liquid crystal was observed. In that case, the mesophase could not prevent a diffusion-controlled aggregation of particles. They aggregated according to an isotropic fractal-like growth mechanism (Figure 3a). When the reduction of the platinum acid into platinum metal was obtained by a slower chemical reduction (bubbling of 1 atm carbon monoxide) of  $\text{Pt}^{\text{II}}$  or  $\text{Pt}^{\text{IV}}$  (0.1-0.2 M), the colour of the phase gradually changed from yellow to dark purple and the liquid crystal became less viscous as the reaction proceeded. TEM studies show fibrils composed of a self-assembly of monodisperse platinum particles of 2 nm (Fig. 3b inset). These aggregates remained stable upon extraction and washing. The fibrils exhibit a good uniformity in diameter. The diameter and the length of the fibres lie in the range of 8-20 nm and 0.2-0.7  $\mu\text{m}$ , respectively. The X-ray photoelectron spectroscopy (XPS) analysis confirmed the total reduction of platinum but reveal some traces of remaining surfactants after extraction and washing. Hence, the confinement provided by the SLC led the particles to aggregate with a preferential orientation instead of the 3D isotropic fractal growth observed in the destroyed SLC. It is worth noticing that the progressive disappearance of the platinum acid, along with the progressive acidification of the solution due to the

reduction of platinum, decreased the stability of the SLC in the final steps of the reaction. SAXS shows an effective loss of crystallinity of the mesophase at the end of the reaction.

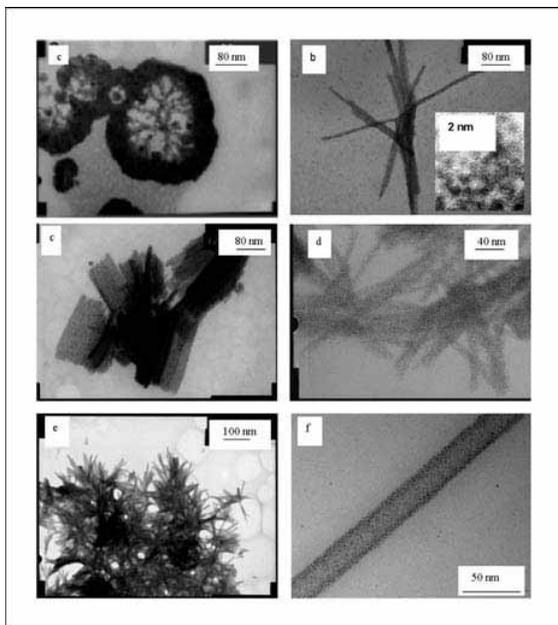


Figure 3 TEM images of nanostructured materials obtained by a) gamma reduction and b) CO reduction of platinum salts (0.1M) in SDS based hexagonal SLC, inset: HRTEM image showing the individual nanoparticles, c) in lamellar SLC (Pt 0.1 M), in SDS based SLC doped with d) Pt:Co (3:1), e) Pt:Pd (1:1) f) in CpCl based SLC doped with Pt (0.1M)

With CO reduction, nanofibres are obtained. We believe that, because the triangular space between three organic cylinders defines a less constrained region than the direct inter-cylinder space, it presumably drains the metallic nanoparticles as they form upon reduction of the platinum salt. This would lead to their one-dimensional aggregation along a direction parallel to the cylinder main axis.

The UV-visible spectrum obtained from Pt fibres diluted in isopropanol after washing is shown Figure 4. This spectrum displays a maximum absorption at 540 nm, which is different from the known plasmon of spherical Pt-nanoparticles located around 215 nm.<sup>14, 15, 16</sup> Its shape is probably due to the rod-like Pt structure and to the interparticle-coupled plasmon exciton.

The structuring effect of the SLC geometry on the metal nanoaggregates morphology was unambiguously confirmed by similar syntheses performed with an SLC designed with a lamellar structure formed by the addition of a slight excess of 1-pentanol to the previously used hexagonal SLC. In this case, slabs of platinum made of

aggregated nanoparticles are obtained, which also remain stable after extraction (Figure 3c).<sup>7,16</sup>

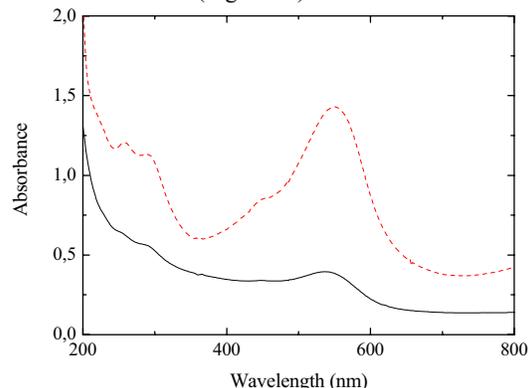


Figure 4. UV/Vis spectra of Pt nanofibers obtained by CO reduction of platinum salts ( $H_2PtCl_6$ ) in hexagonal SLC/Pt (0.1 M); the fibers were diluted in isopropyl alcohol after washing.

This process was also extended to different metals. The syntheses performed with palladium,<sup>7</sup> tin-doped platinum,<sup>7</sup> platinum-cobalt (Figure 3d) and platinum-palladium (Figure 3e) demonstrate from their morphology variations that the nature of the metal precursor can also alter the final morphology of the aggregate, depending on the initial size of the pristine nanoparticles and the competitive mechanisms between metal framework growth and particle aggregation. Figure 3c – 3f displays some of the TEM images of typical fibres or lamellae obtained using doped SLCs containing  $H_2PtCl_6$  alone or mixed with  $PdCl_2$  (0.05 M),  $CoSO_4$  (0.025M).

### 3. Stability of CpCl based hexagonal phases

We also prepared SLCs by employing single-chain cationic surfactants CpCl and CTAB. Swollen hexagonal phases can equally be obtained with the cationic CpCl and CTAB surfactants. However, to stabilize SLCs prepared with different surfactants, the molar ratio of co-surfactant over surfactant has to be adjusted: it is of the order of 1.4 for SDS, 1 for CpCl, and 0.7 for CTAB. This is the direct consequence of the fact that different surfactant molecules are expected to form films with different spontaneous curvatures. Moreover, we noted that the lattice parameters of samples made with SDS, CpCl, or CTAB were all equal.<sup>8</sup> The fact that the lattice parameters are similar suggests that all structural parameters are of the same order of magnitude as for SDS-based SLCs. Our studies have also shown that hexagonal SLCs can also be obtained when replacing cyclohexane by decane and/or 1-pentanol with 1-decanol.

The use of cationic surfactants allows one to overcome the problem of stability of SLCs in acidic conditions observed with SDS.<sup>8</sup> Our studies have shown a remarkable stability of cationic surfactant based systems, suggesting that an acidic

medium does not modify the hydrophilic interaction of the polar head of CTAB and CpCl.

#### 4. Platinum nanotubes synthesized in CpCl based hexagonal phases

Doped hexagonal phases with high concentration (0.05 to 0.2 M) of platinum and palladium salts were obtained.

It was interesting to note that in case of cationic surfactant (CpCl) the SLC retained their hexagonal symmetry after irradiation *e.g.* CpCl based mesophases doped with platinum salts ( $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ ) were hexagonal before and after gamma or UV irradiation. The TEM images of the reduced phases show platinum nanotubular structures (Figure 3f).

The stability of SLC based on cationic surfactants at acidic pH make them promising nanoreactors for metal nanostructure synthesis. Experiments with these systems are still in progress

#### CONCLUSION

We have investigated the stability of swollen hexagonal phases with respect to modifications of the chemical nature of the components and of the pH and have shown that they can be prepared in a wide range of experimental conditions without changing their structural parameters. The stability and versatility of these SLCs make them very promising nanoreactors. Metallic nanomaterials of different shapes (fibres, tubes or lamellae) can be synthesized using these SLCs as soft templates. The symmetry of the swollen liquid crystals can also act as template to organize self-assemblies of nanoparticles into larger controlled shapes.<sup>16</sup>

Physical properties of these new nanomaterials and their potential application in catalysis and electrocatalysis are under investigation.

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