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Formation of assembled silver nanowires by reduction of silver thiolate in polyol/toluene medium†

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Reduction of silver nitrate in polyol/toluene biphasic medium containing dodecanethiol led to organised silver nanowires, results of an interaction between silver nanoparticles and the layered phase $AgSC_{12}H_{25}$.

Many efforts have been made during the last decade to develop new synthetic routes to monodisperse metal nanoparticles. This is especially true for gold and silver particles for their optical properties. Several physical[1,2] or chemical processes[3,4] and even alternative sources such as biological systems[5] have been investigated. Moreover, anisotropic particles are often desired for their optical properties which differ strongly from those of spherical particles. Several methods have been studied to control the anisotropic growth of the metal from a solution : the use of solid host templates, such as alumina membrane,[6] mesoporous silica[7,8] or carbon nanotubes,[9] the use of rod-like micelles,[10] or photoreduction.[11] 1D alignments of silver and gold nanoparticles on patterned surfaces such as carbon[12] or alumina[13] have been obtained. Self-assembly of silver nanocrystals into 2D nanowire arrays has also been described,[14] for which the anisotropy of the particles was assumed to be the driving force of the directional assembly.

Besides the liquid phase processes, chemical routes involving a solid phase with Au(I) or Ag(I) ions linked to a long chain amine or carboxylate were also investigated.[15–17] UV irradiation or thermal decomposition were then used to produce metal, and under mild conditions, anisotropic morphology or assembly could be obtained.[15] The interest of these solid phases lies in the fact that they present several phase transitions in the temperature range below 200 °C.[18] The silver thiolates $AgSC_nH_{2n+1}$ present a layered structure at room temperature with the sulfur atom linked to three silver ions.[19] At higher temperature they behave as thermotropic liquid crystals, the number of phases and the transition temperatures depending on the number of carbon in the alkyl chain. The silver thiolate $AgSC_{12}H_{25}$ was found to undergo a phase transition toward a hexagonal columnar mesophase at 130 °C. In this phase, the thiolate ions are linked to two silver ions forming disk-shaped octanuclear species that stack in columns.[18]

This work describes the reduction of silver nitrate by a liquid polyol in presence of dodecanethiol in a biphasic 1,2-propanediol/toluene medium. Silver spherical nanoparticles and nanowires have been obtained. The wire formation is found to be templated by the silver thiolate solid phase that is formed during the reaction. Reduction of silver nitrate in liquid α-diol has proven to be a suitable method for the synthesis of silver monodisperse particles in the nanometre size range,[20] and anisotropic particles in the micro- and nanometre size range.[21,22] In that method the liquid polyol acts both as solvent for the metal salts, reducing agent and medium of growth of the metal particles. In order to control the growth step and then the particle morphology, poly(vinylpyrrolidone) (PVP) was used.[20–22] Metallic silver anisotropic growth was induced by heterogeneous nucleation by seeding the solution with platinum nuclei.[21–22] In this work, the dodecanethiol was used to control the growth step and prevent from the agglomeration of the silver particles. A synthesis of gold nanoparticles by reduction in a biphasic water/toluene medium has already been developed by Brust *et al.*[3] In contrast to that method, no phase transfer agent was used here, toluene and 1,2-propanediol being very slightly miscible at room temperature and highly miscible at the boiling point of the mixture. In a typical experiment the silver nitrate was dissolved in 1,2-propanediol and 0.5 equivalent of dodecanethiol was dissolved in toluene. The mixture of these two solutions was heated to reflux for one hour, and then cooled down slowly to room temperature. The polyol solution remained colourless while the toluene solution turned orange-red indicating the presence in this phase of metallic silver particles. A solid phase was also found in suspension in toluene.†

The UV–visible absorption spectrum of the toluene solution displays a symmetrical peak located at 450 nm that corresponds to the surface plasmon resonance of metallic silver nanoparticles coated by dodecanethiol.[23] Transmission electron microscope (TEM) studies on the solutions showed spherical silver particles in the nanometre size range.

Scanning electron microscope studies on the solid phase showed a fibrous morphology with fibers diameters of about 100 nm (Fig. 1). TEM studies showed different kinds of fibers. Metallic wires with diameters in the nanometre size range and length varying from several tens of nanometres to several tens of micrometres were observed. Some fibers are made up of 6 nm mean diameter wires arranged in 2D arrays with a regular interwire spacing of 1.5 nm (Fig. 2a). High resolution transmission electron microscopy revealed metallic silver planes (Fig. 2a) and showed the polycrystalline texture of the wires (Fig. S1, ESI†). Alignments of silver particles in a non

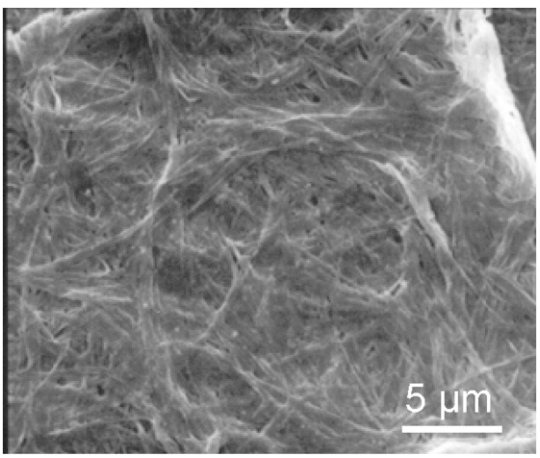

Fig. 1 SEM image of the solid phase Ag(0)/AgSR prepared by reduction of silver nitrate in polyol/toluene medium in presence of dodecanethiol.

† Electronic supplementary information (ESI) available: experimental and spectroscopic data. See http://www.rsc.org/suppdata/cc/b3/b304021f/

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metallic phase, before coalescence, were also evident (Fig. 2b). Thus, the wires are formed by coalescence of primary nanoparticles. Unidirectional organisations (wire or alignment) are not observed in all fibers; some of them are made up of spherical nanoparticles embedded in a non metallic phase as was previously described for gold particles in a Au(I)-amine solid phase.[15]

The solid phase recovered is found partially reduced and contains both metallic silver and silver thiolate. The UV–visible absorption spectrum of the solid phase displays absorptions at 330 nm and at 420 nm (with in most cases a shoulder towards red wavelengths) corresponding to the unreduced silver thiolate $Ag(I)SC_{12}H_{25}$ and to metallic silver nanoparticles, respectively (Fig. S2, ESI†). Thermal differential analysis shows an endothermic peak close to 130 °C characteristic of the phase transition from lamellar crystalline to columnar mesophase of the silver thiolate $Ag(I)SC_{12}H_{25}$.[18] It is noteworthy that this peak is always found at a temperature lower than 130 °C that can be interpreted as the result of a strong interaction between the silver thiolate and the metallic wires and spheres (Fig. S3, ESI†). The X-ray diffraction (XRD) pattern of the solid phase recovered in the synthesis presents in most of case the (0*k*0) lines (Fig. S4, ESI†) corresponding to the layered structure of the silver thiolate $Ag(I)SC_{12}H_{25}$ with an interlayer spacing b = 35,0 ± 0,1 Å.[19]

The scheme of formation of the silver particles and wires can be described as follows. The silver nanoparticles are formed by reduction in the polyol/toluene medium at high temperature. The size in the nanometre range is controlled by the presence of 0.5 equivalent of dodecanethiol in solution. After one hour at the boiling point the reduction is not complete, a fraction of Ag(I) is complexed by the dodecanethiolate that makes it more difficult to reduce. At high temperature the silver thiolate $Ag(I)SC_{12}H_{25}$ is soluble in toluene but when the medium is cooled down it precipitates. The metal particles coated by dodecanethiol are soluble in toluene and some of them are trapped in the silver thiolate phase when it precipitates. Thus, at the end of the reaction the toluene solution contains spherical particles coated by dodecanethiol and a solid phase made up of metal particles embedded in the silver thiolate. With ageing a 1D coalescence of the metal particles takes place. Although it is not fully understood yet, the coalescence of particles into wires appears templated by the silver thiolate phase. The columns made up of octanuclear species in the columnar mesophase[18] cannot explain the nanometre size wires shown in Fig. 2a. The diameter of these columns is very small and the silver concentration in our experiment is very far from the pure solid state. Actually, such wires were not observed by reduction of the silver thiolate in solid state, even above 130 °C. It is probably the lamellar phase when it precipitates in the polyol/toluene mixture that acts as template for the anisotropic growth. Thus, a mechanism by formation of tubular structures as templating agent by analogy with lipid self-organisation may be suggested.[24] The conditions of exfoliation of the lamellar $Ag(I)SC_{12}H_{25}$ in a polyol/toluene mixture is under investigation.

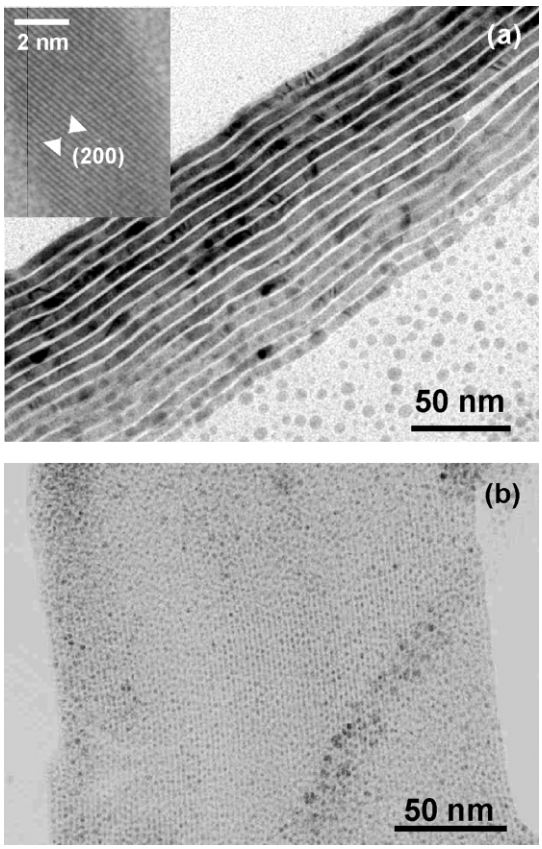

Fig. 2 TEM images showing the texture of some fibers (a) 6 nm nanowires; (b) 1D alignment of 2 nm sized nanoparticles. *Inset :* HRTEM image of a wire showing (200) metal silver planes.

In conclusion, a new method of synthesis of metallic nanowires has been developed and a mechanism has been suggested. The novelty of these wires lies in their small diameter and in their organisation. The solid phases obtained reflect the organisation within the native hexagonal mesostructured silica, provided by the inversion of the organic and inorganic moieties. These experiments are promising for the synthesis of well-defined 2D and 3D organisations of metal nanowires.

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