Self-organization on surfaces/Auto-organisation sur les surfaces

Organometallic approach to nanoparticles synthesis and self-organization

Bruno Chaudret

Laboratoire de chimie de coordination CNRS, 205, route de Narbonne, 31077 Toulouse cedex 04, France

Available online 12 January 2005

Presented by Guy Laval

Abstract

The use of organometallic precursors allows the synthesis in mild conditions of metal nanoparticles displaying a controlled size, shape and surface environment. This method has been extended to the synthesis of bimetallic magnetic nanoparticles of controlled anisotropy and of semi-conducting oxides. We have furthermore demonstrated recently the ability of these particles to change their size or shape according to the properties of the surface ligands present. This review will focus on the organometallic approach developed in Toulouse towards the synthesis of the particles and the demonstration of the presence and role of the different ligands in the chemistry of the particles. In a second step, we describe the role of Coordination Chemistry to orientate the growth of the particles to control their monodispersity and their shape (spheres, rods, cubes, wires). A special point will be devoted to the self-organization of the particles and to the formation of 3D super-lattices of nanoparticles, a true crystallization process. Finally, some applications in physics and microelectronics will be described. *To cite this article: B. Chaudret, C. R. Physique 6 (2005).*

Résumé

Approche organométallique à la synthèse et à la auto-organisation de nanoparticules. L'utilisation de précurseurs organométalliques permet la synthèse de nanoparticules métalliques dans des conditions très douces de température et de pression. La taille, la forme et la surface des particules peuvent ainsi être contrôlées. Cette méthode peut être étendue à la synthèse de nanoparticules bimétalliques, par exemple d'anisotropie magnétique contrôlée, ou de nanoparticules d'oxydes semi-conducteurs. Nous avons démontré la possibilité pour ces particules de changer de taille et de forme en solution en fonction des propriétés des ligands organiques utilisés. Cet article de revue présente la méthode de synthèse organométallique utilisée à Toulouse et fait apparaître l'importance des ligands pour contrôler la chimie de surface des particules. De plus, ces ligands permettent de contrôler l'étape de croissance pour conduire à des nanoparticules monodisperses de formes variées (sphères, cubes, bâtonnets, fils). Nous décrivons également l'auto-organisation de ces particules et la formation de super-réseaux en 2 ou 3 dimensions. Quelques applications de ces nanoparticules sont brièvement décrites. *Pour citer cet article : B. Chaudret, C. R. Physique 6 (2005).*

E-mail address: chaudret@lcc-toulouse.fr (B. Chaudret).

1. Introduction

The synthesis of gold particles has been known since the Romans. Such particles have been used either for medicinal purposes or for their intense colour (blue-purple-pink). After the classification by Lavoisier of elements and oxides, controversies appeared regarding the real nature of the purple solutions of gold. This was for example attributed to the 'purple gold oxide' by Fourcroy at the end of the XVIIIth century [1]. The discovery by Faraday of 'colloids' formation through reduction of gold salts by phosphorus launched a research area which became very popular through the first half of the XXth century [2]. In order to precisely characterize these colloids, very ingenious techniques were developed, such as 'ultramicroscopy'. This allowed Zsigmondy to determine the size of nanoparticles present in a gold hydrosol, namely 15 nm, which was later confirmed [3].

Nanoparticle synthesis then remained largely in the hands of physical chemists who, besides the use of physical techniques such as atom evaporation, have developed techniques based on salt reduction or compound precipitation (oxides, sulfides, selenides, . . .) associated, in general, to a kinetic control of the reaction using high temperatures, slow addition of reactants or use of micelles as nanoreactors [4]. This method can lead to nanoparticles of controlled size and shape which may self-assemble into super-crystals after size selection [5]. An interesting variation of the reduction method consists in using polyols both as solvent and reducing agents. This has in particular been developed by Fiévet and allows the formation of monodisperse metal nanoparticles able to self-organise on surfaces [6].

Günter Schmid has developed early in the eighties an approach based on the use of boron hydride for synthesizing a 'giant gold cluster': $Au_{55}Cl_6(PPh_3)_{12}$ [7], and has since then pursued the chemistry and physics of such clusters. Other organometallic approaches based on the kinetic control of the high temperature decomposition of carbonyle complexes have been developed by the groups of Bawendi [8], Sun [9] and Alivisatos [10].

At the end of the 1980s, after having developed very mild conditions for the synthesis of unstable dihydrogen complexes [11], we reasoned that these conditions (room temperature, low gas pressure) could allow the control of the growth of very large organometallic clusters or very small nanoparticles. The advantage of organometallic chemistry would lie in the precise control of the reaction conditions and therefore of the *surface of the particles*, namely absence of oxidation, number and nature of surface species (ligands). Other advantages could be the control of the surface reactivity and stepwise growth of the clusters. Furthermore, we thought that the particles could be characterized both by techniques usual in the field of nanomaterials (TEM, HRTEM, SEM, XRD, WAXS, XPS) and by techniques derived from molecular chemistry (spectroscopies: IR, UV, NMR in solution and in the solid state; magnetic measurements).

This approach was indeed successful for the synthesis of mono- and bimetallic nanoparticles as well as oxides but a number of questions were raised which we will try to answer in the present review, namely:

– Can the nano-objects prepared by this approach be compared for their physical and chemical properties to aggregates prepared in ultra high vacuum?
– On the other hand, can these objects be considered as giant molecular clusters in terms of various types of ligands coordination and surface chemistry?
– Is it possible to assemble these nanoparticles through different techniques of self-assembly and, better, is it possible to crystallize super-structures of nano-objects?
– Does organometallic chemistry allow a shape control of the nanoparticles?
– Are these objects pertinent for applications in microelectronics and nanoelectronics?

These points will be developed here below together with an additional one, the synthesis of oxide nanoparticles, which follows procedures somewhat different from those commonly used for metal particles.

2. Organometallic synthesis of metal nanoparticles

The synthesis procedure consists in removing the ligands from an organometallic complex in the mildest possible conditions (room temperature or below, low gas pressure) and with the minimum of potentially pollutant reactants. The ideal case is the reaction of an olefinic precursor with dihydrogen which leads to the production of an alkane unable in these conditions to produce strong bonds with the growing metal surface [12]. The 'naked' atoms produced in these conditions will condense to produce nanoparticles. When the stabilizer is a polymer, only few electronic interactions will exist between the polymer and the particle which may therefore display physical properties similar to what can be observed in vacuo or even in the gas phase (see below the magnetic properties of cobalt nanoparticles). Another approach can be the displacement of the surface ligands by a reactive gas such as CO, leading to unstable intermediates which will eventually condense into particles. In the latter case however, CO will always be present at the surface of the growing clusters which will modify their chemistry. The reaction
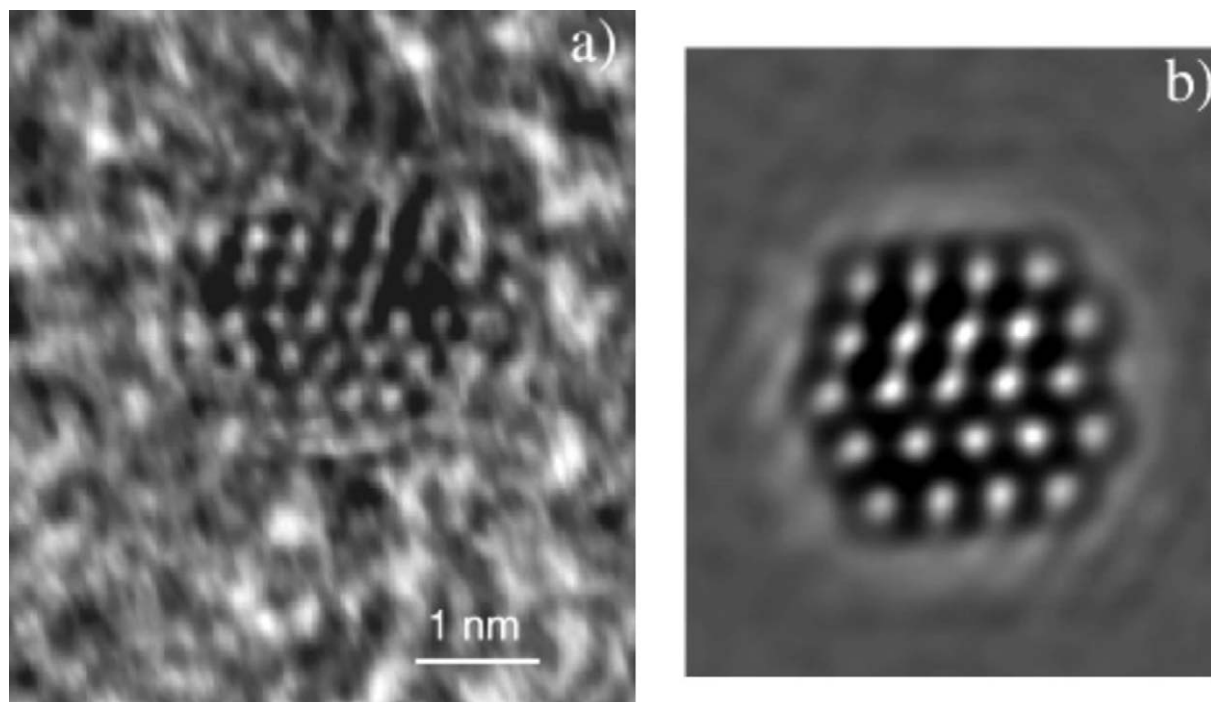
Fig. 1. (a) High resolution electron micrograph of a Pt–Ru$_3$ nanoparticle; (b) image simulation.

conditions (temperature, gas pressure, concentration of precursors and stabilizers) will have a strong influence on the nature of the particles formed and first on their size.

2.1. Structure

Using a polymer which will act as a sterical stabilizer for the growing particles, we could synthesize a number of nanoparticles of various types of (Fe, Co, Ni, Ru, Rh, Pd, Pt, Cu, Ag, Au, In) as well as bimetallic (Pd–Cu, Ru–Pt, Co–Ru, Co–Rh, Co–Pt) [12]. Typically olefinic precursors (Ru(η^4-C$_8$H$_{12}$)(η^6-C$_8$H$_{10}$), Co(η^3-C$_8$H$_{13}$)(η^4-C$_8$H$_{12}$), Pt(dba)$_2$, . . .) are hydrogenated which leads to nanoparticles of 1 to 3 nm mean size according to the reaction conditions (essentially relative concentration of precursors and polymers, temperature and gas pressure). At these small sizes, the particles generally adopt the structure of the bulk element (Ru: hcp [13]; Ni, Pd, Pt: fcc [14]) with the exception of cobalt which displays a polytetrahedral structure similar to cobalt ε [15]. The bimetallic nanoparticles can either form an alloy at all compositions when the elements display the same bulk structure (Pd–Cu) [16] or lead to structural changes as a function of particles composition [17] or even to segregated structures [18]. The most spectacular case is that of the Ru–Pt particles [17]. A dissolution of ruthenium into the platinum lattice is observed up to the critical composition Pt–Ru$_3$ which indeed corresponds to the limit of solubility of ruthenium into the platinum lattice in the bulk (Fig. 1). Before this composition the particles are fcc and at higher Ru content they become hcp. At the critical composition, the particles are strictly monodisperse, very small and display a twinning plane in the equatorial plane of the particle corresponding to a hcp stacking fault in an fcc particle.

These results demonstrate that this synthetic technique leads to crystalline well-ordered particles with two noticeable and interesting exceptions: indium particles which are 'liquid' at room temperature [19] and polytetrahedral cobalt particles [15].

2.2. Infrared spectroscopy

In order to test the clean, unoxidized nature of the nanoparticle surfaces, we used first CO as a probe molecule to evaluate the electron density at their surface. It has been demonstrated that the CO stretching frequency values measured by infrared spectroscopy in solution was in good agreement with the values measured on aggregates in ultra-high-vacuum. The presence of some surface oxidation leads to an important shift of this value towards high frequencies. In palladium nanoparticles, a correlation has been established between the ratio of linear to bridge CO groups and the size of the particles [20]. For bimetallic Pd–Cu particles, a surface reconstruction was observed at room temperature [16]. Thus, under vacuum, there is an enrichment

of the bimetallic particles surface in Cu. Upon addition of CO, the IR spectrum displays bands attributed to CO on Cu. However, the particles slowly evolve at room temperature and the IR spectrum shows after several hours a typical spectrum for CO on Pd, hence evidencing the enrichment in Pd of the particles surface. After placing the particles in vacuo overnight and adding again CO, a typical spectrum for CO on Cu is again visible which shows the reversibility of this surface reconstruction.

These simple experiments demonstrate the clean, unoxidized character of the nanoparticles together with their surface dynamic at room temperature.

2.3. Magnetic measurements

In the case of iron, cobalt and nickel, as well as their alloys, the most sensitive technique for characterizing the particles surface is the measurement of their magnetic properties. Thus, we have synthesized cobalt nanoparticles of 1.6 nm (ca 150 atoms), 2 nm (ca 300 atoms) and 4 nm (a few thousands atoms) mean size. The structure of the particles is hcp in the latter case and polytetrahedral in the two other cases. The 4 nm particles display a saturation magnetization equal to that of bulk cobalt (1.72 μ_B) whereas the smaller particles do not saturate at 30 T. They display furthermore a saturation magnetization higher than the bulk one (respectively 2.1 and 1.9 μ_B/cobalt atom at 30 T for particles of 1.6 and 2.0 nm) [21]. These results are very similar to those of Billas et al. on time-of-flight clusters in ultra high vacuum [22]. This suggests a direct correspondence between the physical properties of gas phase aggregates and those of prepared in solution using the organometallic approach. In a similar way, bimetallic Co–Ru, Co–Rh and Co–Pt nanoparticles of low size dispersity and define compositions have been synthesized. These species, and specially the Co–Rh particles, also display a very important excess of magnetization compared to the values found in the bulk alloy. This is attributed in the Co–Rh case to the strong polarization of Rh in the vicinity of Co, probably because of the difference of structure between the bulk and the particles although this is not totally understood at the present time [18].

These experiments have recently been extended to the case of iron. The synthesis of small Fe particles has long been difficult due to the lack of suitable precursor. However, using the complex $Fe[N(SiMe_3)_2]_2$ ($Me = CH_3$) as precursor, we have obtained nanoparticles of low size dispersity and displaying a magnetization at 5 T higher than in bulk iron and comparable to that of gas phase aggregates [22,23].

In order to validate the results obtained on our particles, we reacted them with various ligands and/or contaminants and measured their magnetic properties again. It was found that surface oxidation or coordination of π-accepting ligands would lead to a strong decrease of the particles magnetization. In contrast, purely σ-donating ligands do not affect the magnetism of the particles [24].

In summary, the experiments carried out evidence a great similarity of properties between polymer protected nanoparticles prepared by the organometallic method and clean aggregates prepared in ultra high vacuum.

3. Surface organometallic chemistry on nanoparticles

An organometallic complex consists of a central metal atom and of a number of ligands which can schematically be classified in 3 groups:

- ancillary ligands, the role of which is to stabilize complexes or nanoparticles and liberate a vacant coordination site when necessary;
- active ligands which may take an important role in the reactivity of the complexes/nanoparticles (e.g. hydrides, alkyl groups, carbenes, . . .);
- directing ligands which will orientate the reactivity of the complexes/particles (for example asymmetric ligands such as DIOP or BINAP).

In order to understand the reactivity of the nanoparticles and to be able to modify them (give them a shape, obtain superlattices), it is important to characterize the surface ligands and their mode of bonding.

3.1. Ancillary ligands

The syntheses described in the preceding chapter can be performed using as stabilizers classical ligands of organometallic chemistry, for example amines, thiols or phosphines, instead of polymers. The amount of ligands added will allow the control of the particle growth and therefore first their size.

Using weak stabilizers such as alcohols leads to the agglomeration of initially produced particles inside droplets to lead to dendritic particles displaying a fractal aspect. Upon varying the nature and the quantity of alcohol used, dendritic polycrystalline

nanoparticles of a few nm to several nm mean size were prepared. A surprising linear correlation was for example established between the amount of alcohol used and the size of the particles in an hexane/methanol mixture [25].

Amines are weak ligands which may easily be displaced from the nanoparticles surface and allow the further growth of nanoparticles through coalescence. This is revealed by solution ^{13}C NMR studies which evidence a fast exchange at the NMR time scale between amine ligands free and coordinated to ruthenium [26]. This study has also been extended to the case of palladium and platinum and the same fluxional behaviour has been observed. By increasing the amine concentration, it is possible to orientate the coalescence of the particles towards the formation of nanorods.

Thiols are firmly attached to the surface of noble metal particles. When coordinated to platinum or ruthenium, we did not observe any fluxional behaviour [26,27] but found the slow catalytic formation of alkyl disulfides due to the coupling of thiolato ligands at the surface of ruthenium [26]. We therefore proposed that thiols react with the surface of the particle to produce thiolate ligands.

3.2. Active ligands

The most important ligand in organometallic chemistry, as far as catalytic reactivity is concerned, is the hydride. Since our synthesis method involves the decomposition of an organometallic precursor and the growth of particles under a dihydrogen pressure, we have attempted to characterize the presence of surface hydrides by a variety of NMR methods. Thus we used solution NMR, gas phase NMR, magic angle spinning (MAS) solid state NMR and static solid state NMR at variable temperature [28]. We found that surface hydrides are indeed present on the ruthenium surface as deduced from solution and gas phase studies. Thus upon placing a sample of nanoparticles in vacuo, no desorption of dihydrogen is observed. However, introducing deuterium in the NMR tube leads to the clean production of H–D hence revealing the presence of surface hydrides. These species can then be observed directly by solid state NMR and display a very high mobility, in agreement with recent theoretical calculations.

3.3. Directing ligands

The coordination of ligands at the surface of metal nanoparticles has to influence the reactivity of these particles. In order to demonstrate this effect, we have used asymmetric ligands and studied the influence of their presence on selected catalytic
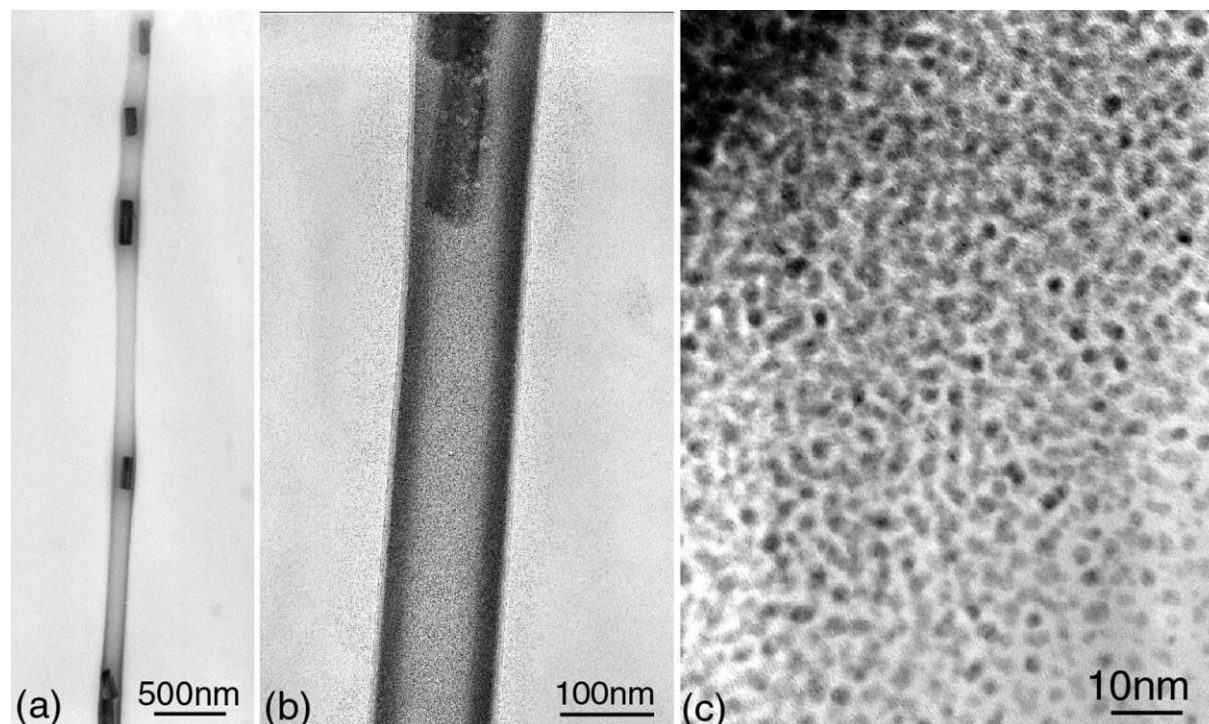

Fig. 2. Transmission electron micrographs of super-structures resulting from the self-assembly of 1.6 nm Pt particles stabilized half by 4-HO–C_6H_4–SH and half by 4-NH_2–C_6H_4–SH at three different magnifications: (a) ×15000; (b) ×100000; (c) ×600000.
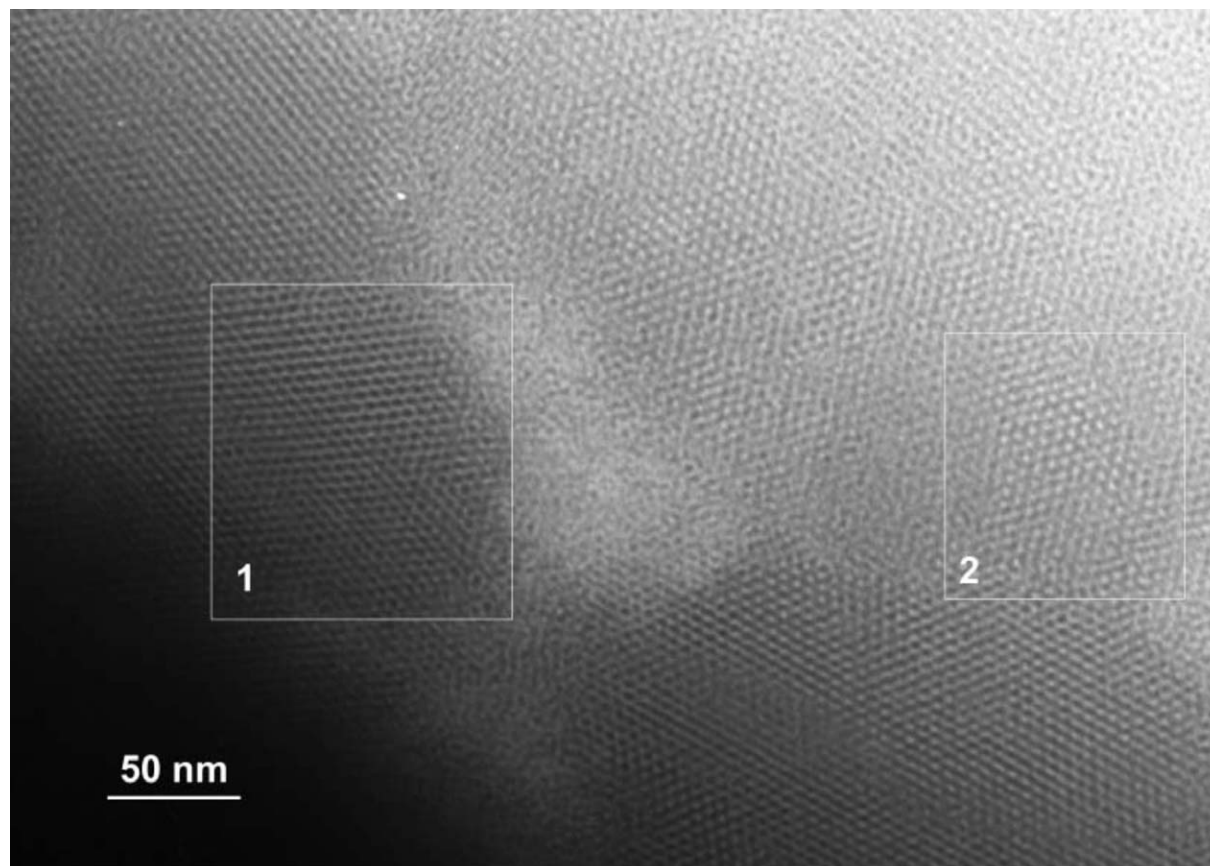
Fig. 3. Transmission Electron Micrograph of self-organized Ni–Fe nanoparticles on a carbon substrate. According to the contrast, different zones are visible: (1) multi-layers; (2) a mono-layer.

transformations. The reaction chosen was an allylic alkylation reaction catalysed by palladium nanoparticles. We found that: (i) the modified nanoparticles are active catalysts but not as fast as their molecular counterparts; and (ii) the modified nanoparticles are extremely selective since they are able to convert only one enantiomer of the initial substrate. Overall we found a different reactivity for nanoparticles as compared to molecular catalysts which demonstrates the occurrence of a true colloidal catalysis [29].

In summary, we found that indeed ligands coordinate at the surface of nanoparticles and that they can be firmly or loosely attached to this surface according to their chemical nature. Furthermore, the ligands influence the reactivity of the metal nanoparticles. This is important in catalysis but, as we will see further in this paper, this is also important for the control of the growth of metal nanoparticles of define size and shape.

4. Organization of nanoparticles

In order to make a practical use of nanoparticles physical properties, whether individual or collective, one has to find the way to address them. If we leave out the near field techniques, this in turn requires that the particles be monodisperse and organized in 2 or 3 dimensions. In order to obtain such organizations, several approaches can be envisaged. It is possible to connect to nanoparticles polyfunctional ligands containing a function strongly bound to the nanoparticles surface (thiol, phosphine) and a function liable to take part in hydrogen bonds (amine, alcohol, acid). A spontaneous organization will result from the formation of a hydrogen bond network. Alternatively, it is conceivable to deposit solutions of monodisperse nanoparticles protected by long chain alkyl ligand on a substrate and let the system dry out. In this case, the Van der Waals forces only will allow the organization of the particles. Finally, upon introducing charges, it is possible to precipitate from a solution of nanoparticles super-crystals in a way similar to a molecular crystallization.
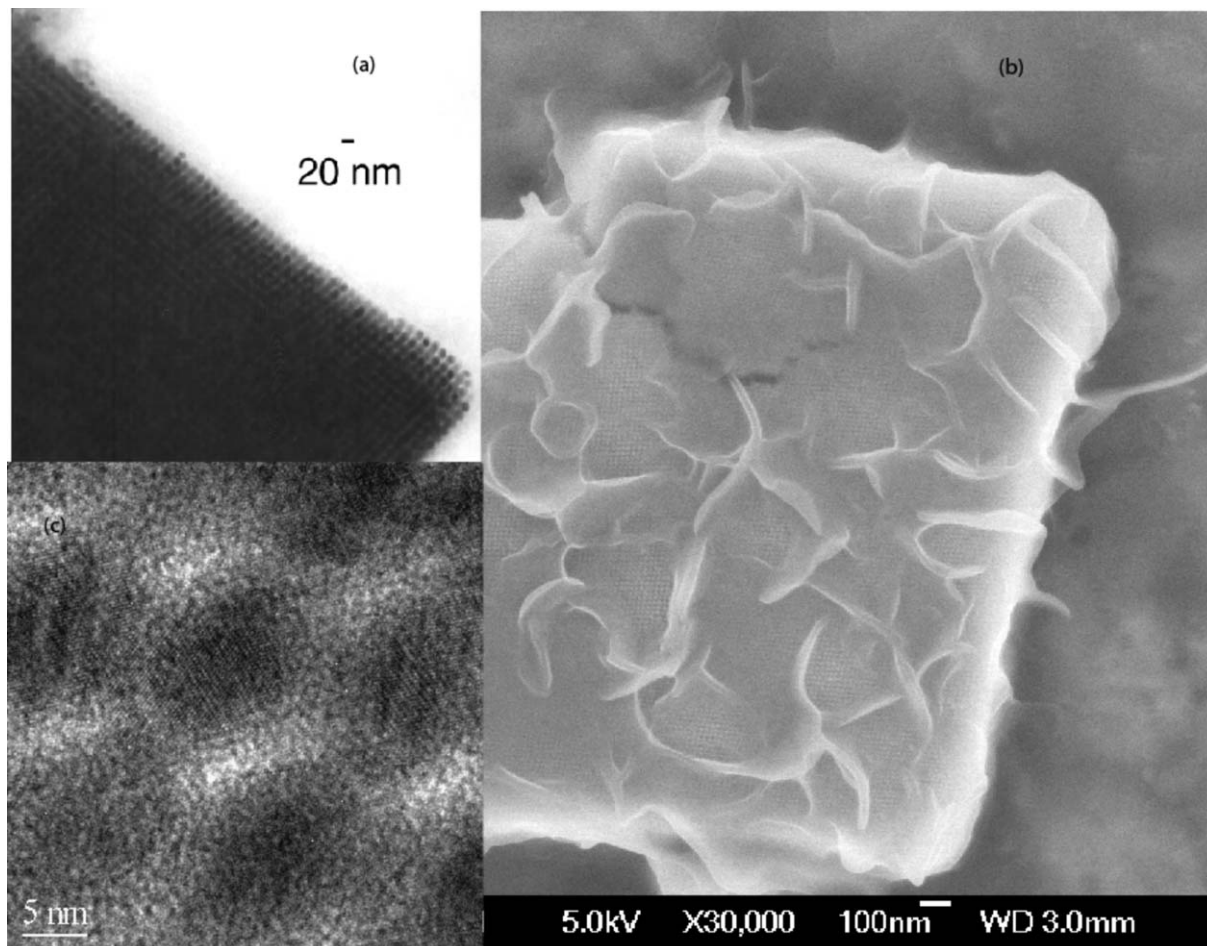
Fig. 4. Formation of crystalline 3D super-lattices of tin nanoparticles: (a) TEM view of a facetted super-crystal; (b) SEM image showing particles included into a super-crystal as well as the organic surrounding; (c) high resolution micrograph showing the alignment of the tin atomic planes inside the super-structure.

4.1. Hydrogen bond network

The first idea is to use techniques which are common in molecular chemistry, namely create hydrogen bond networks. For example, we prepared independently 1.6 nm platinum nanoparticles stabilized by *para*-hydroxythiophenol or by *para*-aminothiophenol. Upon reacting an equimolar mixture of both, extended super-structures were produced as monolayers, nanotubes or 3D super-lattices (Fig. 2) [30]. The walls of the nanotubes consist of one monolayer of self-assembled nanoparticles and reach a length in the mm range. In none of these super-structures have the particles changed size or shape. Other types of organic ligands can lead to interesting monodimensional super-structures [31].

4.2. Spontaneous self-organization

The most common method to prepare nanoparticles super-lattices is to use monodisperse nanoparticles either resulting form a controlled synthesis or from a size selection after synthesis and to let them self-assemble onto various substrates (microscopy carbon grid, silicon wafer, glass, . . .). This generally requires a slow evaporation of a solution of nanoparticles on a flat surface (carbon, silicon wafer). We have employed this technique, not associated with a size selection process, with indium nanoparticles obtained by UV irradiation of organic solutions of InCp (Cp $= \eta^5$-C_5H_5) in the presence of HDA (hexadecylamine, $C_{16}H_{33}NH_2$) [19]. Extended 2D organizations were observed on the microscopy grids upon deposition of a drop of the reaction solution. Using concentrate solutions, solvent evaporation directly produces multilayers displaying a 3D fcc organization. Similarly, Ni–Fe nanoparticles were prepared by thermal decomposition of a mixture of precursors ($Fe(CO)_5$ and $Ni(COD)_2$,
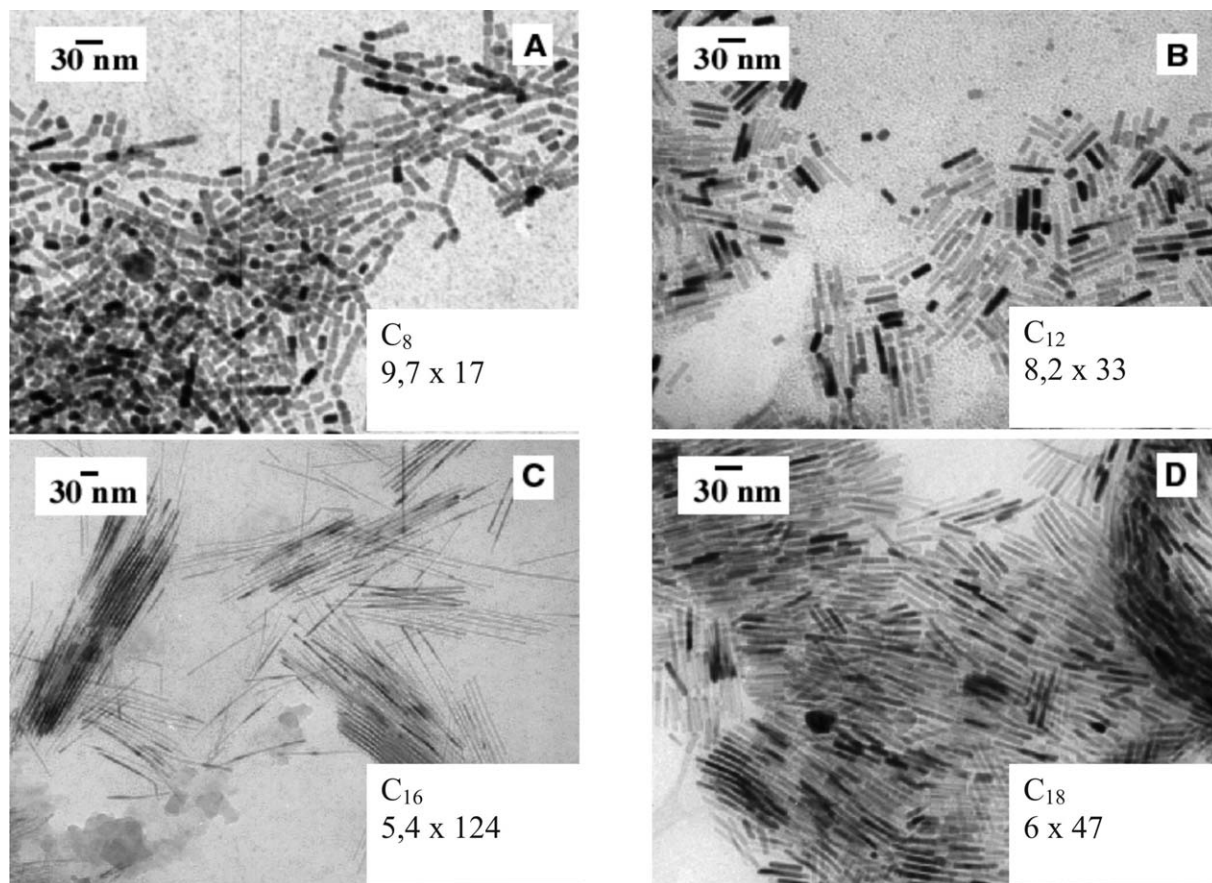
Fig. 5. Cobalt nanorods synthesized in the presence of a mixture of oleic acid and: (A) octylamine; (B) dodecylamine; (C) hexadecylamine; (D) octadecylamine.

COD = C_8H_{12}) in the presence of HDA. They give rise to extended 2D and 3D organisations when deposited on a microscopy grid (Fig. 3) [32].

4.3. Crystallisation

One of the main challenges in the field is the controlled crystallisation of the nanoparticles into 3D super-lattices, similar to artificial opals but including much smaller individual particles. In order to reach this purpose, we have used electrically charged stabilizers (ligands and surfactants). The presence of charges allows a faster agglomeration of the particles and constitution in solution of large super-crystals. For example, the photochemical decomposition of the precursor $[Sn(NMe_2)_2]_2$ in the presence of HDA leads to large cubic particles (ca 100 nm). However, when introducing 10% of the hydrochloride of HAD, HDAHCl, large super-crystals fall out of the solution. The super-crystals are shown to contain monodisperse, slightly ovoid nanoparticles displaying aligned crystalline axes. The space group of the super-lattice is not compact (monoclinic) which is in agreement with a real crystallization of both the particles and their ligand shell (Fig. 4) [33]. This process of crystallization using charges was extended to other systems using as an alternative mixtures of amines and long chain carboxylic acids. In this way, super-lattices of nanoparticles of ZnO, of nanorods of cobalt and of nanocubes of iron were prepared.

In summary, super-lattices may be obtained using the established techniques of self-organization but also a technique derived from molecular chemsitry, the creation of hydrogen bonds networks. In addition, the crystallization of nanoparticles inside 3D super-crystals may be achieved using ionic stabilizers.
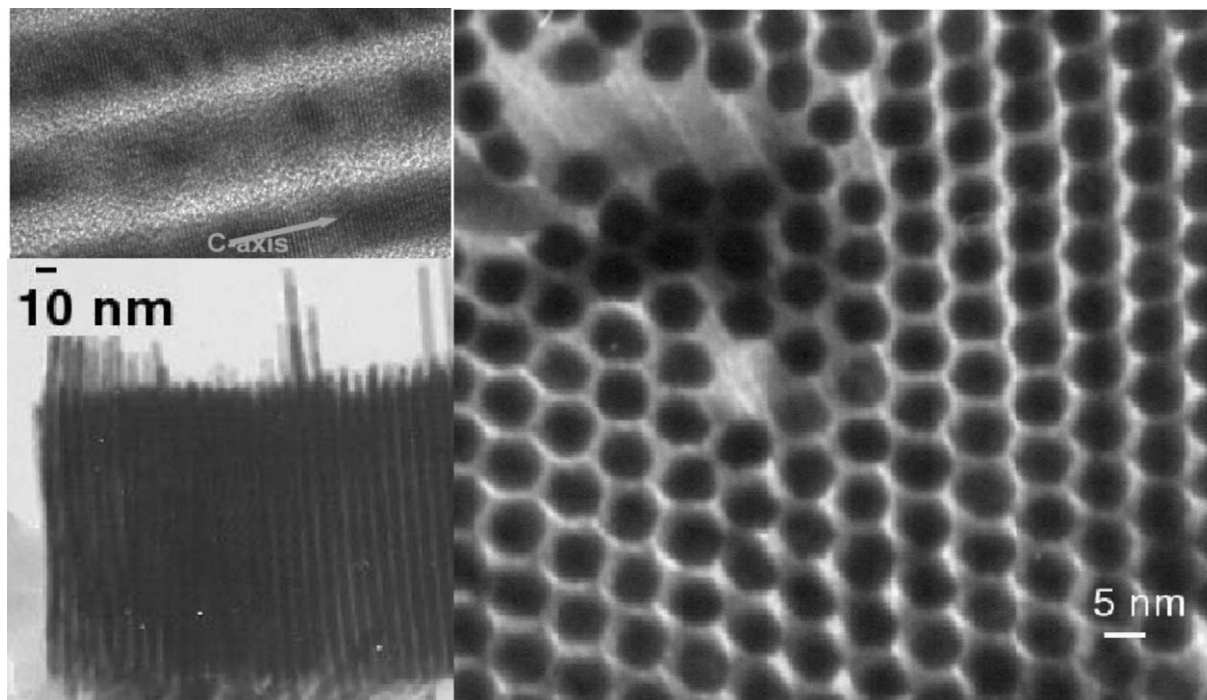
Fig. 6. Super-lattice of cobalt nanorods: (a) top viewheaxagonal; (b) side view; (c) high resolution image.

5. Shape control of nanoparticles

The physical properties of metal nanoparticles are very shape dependent. This is clear for their magnetic properties for which the shape anisotropy term is very important. This is also true for the optical properties of nanoparticles displaying plasmon bands in the visible range (Cu, Ag, Au) and for the luminescence of III–V or II–VI semi-conductors. A particular shape of nanoparticles (nanorods, nanowires, tripods) may also be interesting for connecting them in nanoelectronic devices. In order to achieve this control it is possible to grow the particles inside confined 'host' structures (mesoporous silica, micelles) or to favour a privileged axis of growth through preferred coordination of ligands on selected crystalline faces. Eventually, it is also possible to use ligand mixtures which may act both as growth inhibitors of selected faces and as surfactants to host the growing particles. These ligands mixtures contain typically an amine and a carboxylic acid or an amine an ammonium salt. The ligands are able to react on one another to give rise to catanionic systems. The bonus of the use of such systems is therefore the presence of charges which may favour the formation of super-lattices.

5.1. Confinement in a mesoporous silica

The synthesis of nanoparticles can be carried out using a mesoporous silica as a templating agent. However, even in this case, the functionalization of the pores with organic derivatives is necessary to obtain a good dispersion of the nanoparticles within the silica matrix [34]. As an example, decomposition of Ru(COD)(COT) by dihydrogen may occur inside or outside the pores of a mesoporous silica. However, if the pores are functionalized with phosphonte groups which may act as wek ligands for ruthenium, the growth of ruthenium occurs selectively within the pores. Furthermore, at a high metal concentration, the growing particles are mobile within the pores and may coalesce to yield encapsulated ruthenium nanorods. In a similar way, indium, gold or platinum nanoparticles may be included in the pores of mesoporous silica [35].

5.2. Use of long chain organic ligands

There is presently only little information on the organization of long chain alkyl molecules such as amines and carboxylic acids in organic solutions. Therefore, it is necessary to gain knowledge about this organization, the technique of choice being small angle neutron scattering. In parallel, we directly explored the influence of these ligands on the growth of metal nanoparticles in solution.
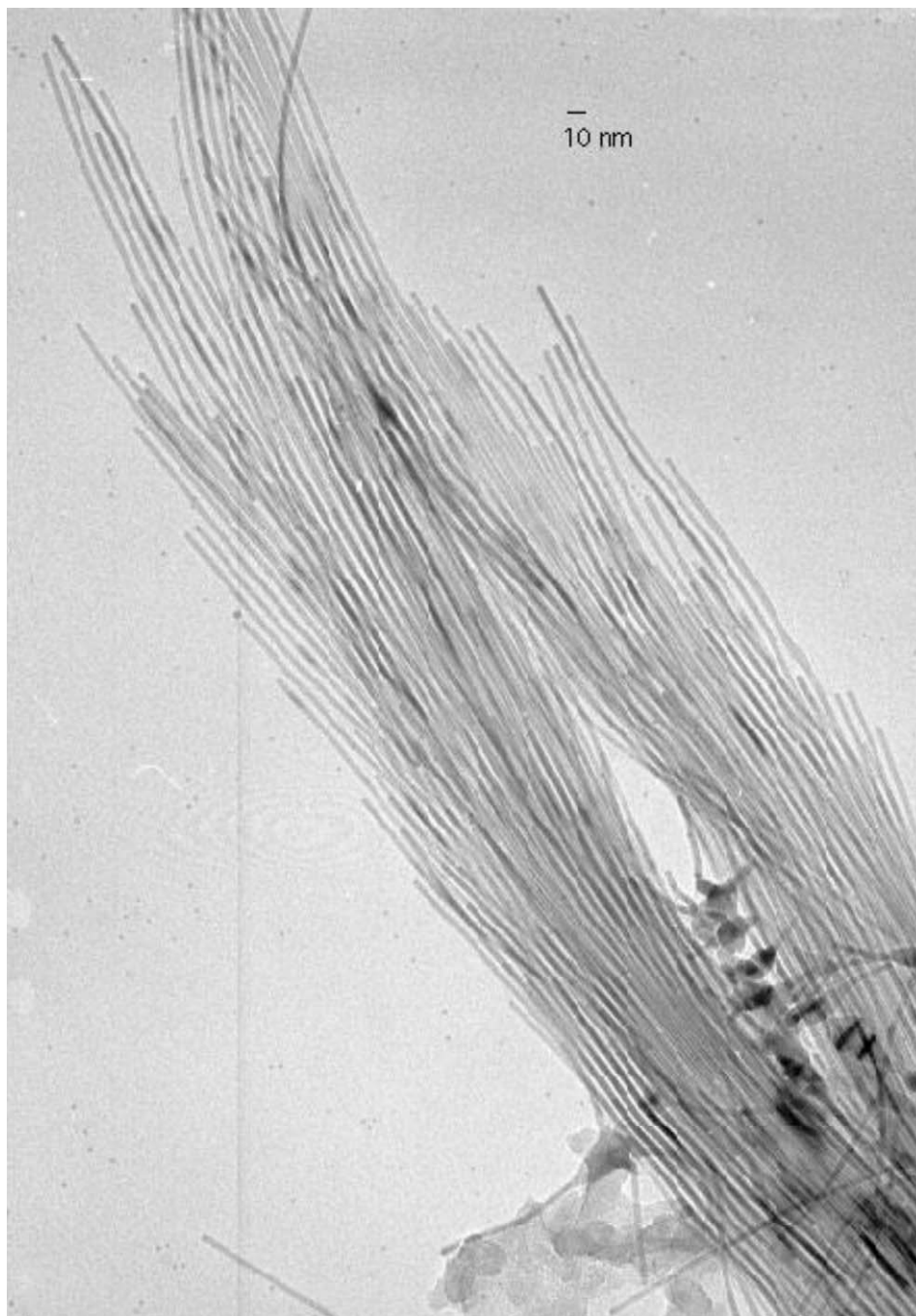
Fig. 7. Transmission electron micrograph of cobalt nanowires.

The decomposition of $Ni(COD)_2$ by dihydrogen in the presence of HDA yields nanoparticles, the aspect ratio of which depends upon the ligand concentration. Thus for 1 or less equivalent HDA, the reaction produces isotropic Ni particles whereas using 10 equivalent HDA, nanorods, monodisperse in diameter, are obtained [36]. The formation of nanowires can also be promoted by a rapid decomposition process. This is illustrated by the decomposition of InCp in the presence of UV irradiation and HDA which leads to very long In bct nanowires [37]. In the case of cobalt, using a mixture of long chain amine and oleic acid, 4 nm isotropic nanoparticles are initially obtained. These particles coalesce at 150 °C under H_2 to give nanorods, the aspect ratio of which only depends upon the chain length of the amine ligand (Fig. 5) [38]. When using stearic acid instead
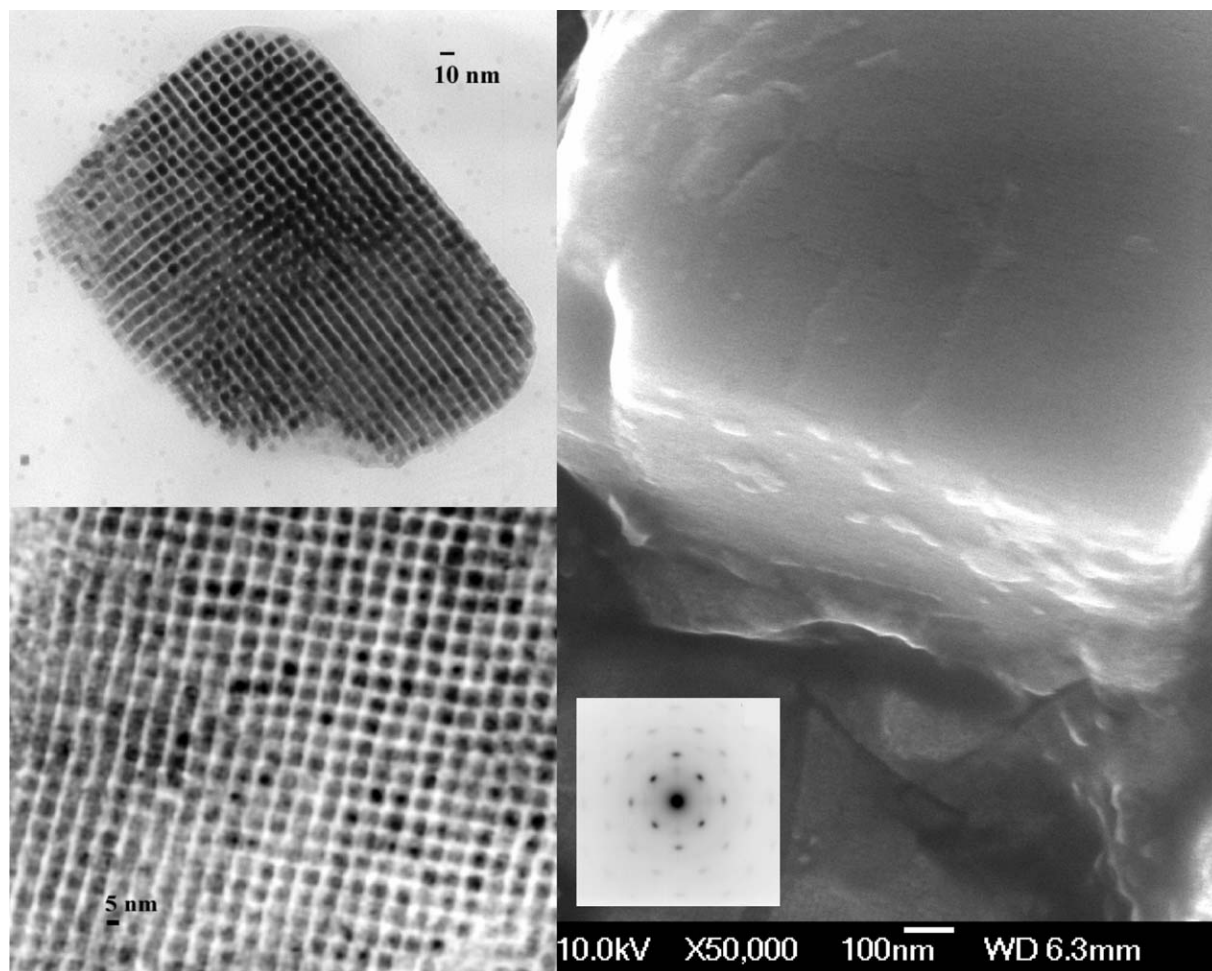
Fig. 8. Super-lattices of iron nanocubes: (a) SEM micrograph of a 'super-cube'; (b) TEM micrograph of a super-lattice; (c) TEM micrograph after ultramicrotomy.

of oleic acid and HDA, all the nanorods formed in the solution self-organize into an unprecedented 2D hexagonal network (Fig. 6) [25]. Whereas the nanoparticles are superparamagnetic, the nanorods are ferromagnetic at room temperature and could in principle be used for magnetic information storage.

Interestingly, a careful study of the particles obtained at the early stage of the reaction by ultramicrotomy shows that most of them are included into 3D crystalline super-lattices [39]. A high resolution micrograph evidences the coalescence of selected particles inside this super-lattice. It is puzzling that the same ligand systems (long chain amine + carboxylic acids) are used for building nanoparticles super-lattices and for controlling the shape of nano-objects. It is therefore possible that the two facts are related and that the anisotropic shape of the particles is due to their growth within the super-lattice created by the self-organization of the particles in a way similar to that observed in mesoporous silica. It is also noteworthy that dihydrogen is necessary for the transformation of the initially formed isotropic nanoparticles into nanorods. This presumably results from the surface organometallic chemistry. The presence of dihydrogen should allow through a metathesis reaction the removal of the initially firmly coordinated caboxylate ligands. This would leave surface hydrides which could favour the particle coalescence, like in the case of ruthenium.

The ligand mixture can control not only the aspect ratio of nanorods but also the length of nano-objects. Thus changing the relative ligand ratio from 1:1 in the preceding case to 2 oleic acid: 1 HDA leads to the formation of very long cobalt nanowires, monodisperse in diameter (4 nm) and displaying a length of several hundreds of microns (Fig. 7) [40]. These nanowires are single crystals and single domain as revealed by magnetic holography studies.

This study could be extended to the synthesis of iron nanoparticles. Using $Fe[N(SiMe_3)_2]_2$ as precursor and a mixture of HDA and oleic acid, spherical nanoparticles are initially formed as in the case of cobalt. However, a thermal treatment at
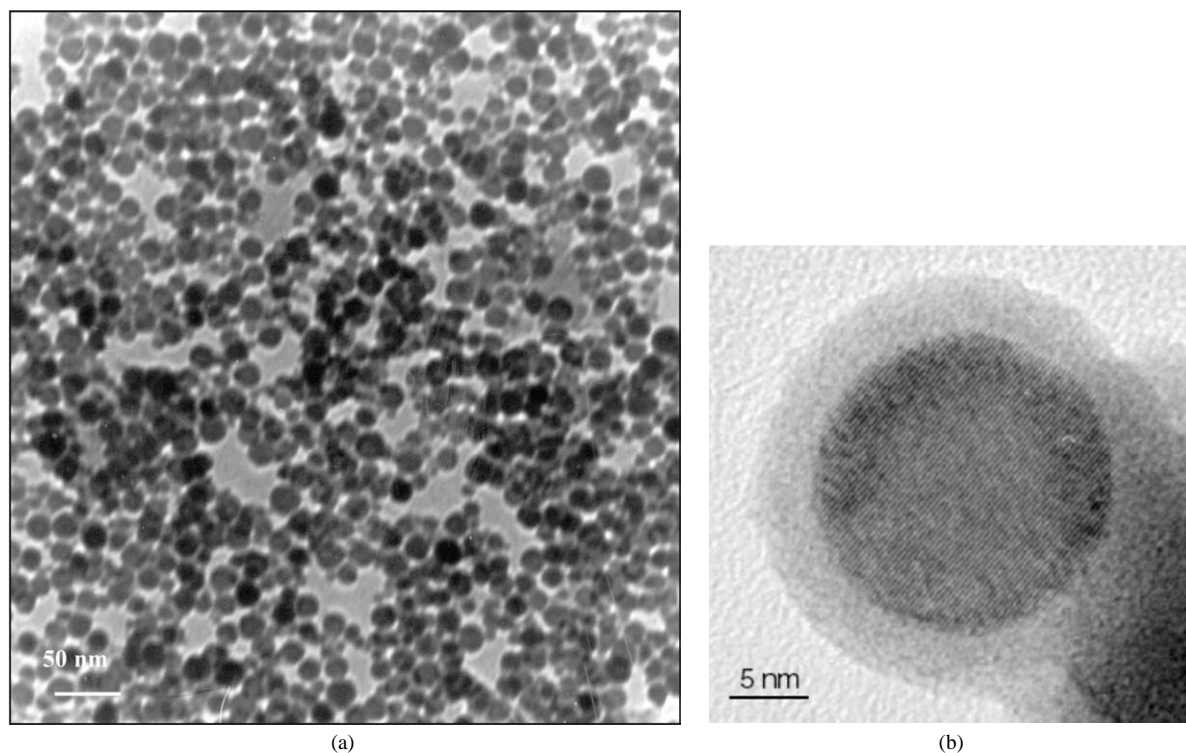
Fig. 9. Core-shell tin/tin oxide nanoparticles: (a) transmission electron micrograph of the particles; (b) high resolution electron micrograph showing the tin core and the tin oxide shell.

150 °C in the presence of H_2 leads to the coalescence of the particles into cubic particles of 7 nm side length. Furthermore, these particles self-organize into cubic super-structures (cubes of cubes; Fig. 8 [41]). The nanoparticles are very air-sensitive but consist of zerovalent iron as evidenced by Mössbauer spectroscopy. The fact that the spherical particles present at the early stage of the reaction coalesce into rods in the case of cobalt and cubes in the case of iron is attributed to the crystal structure of the metal particles: hcp for cobalt, bcc for iron.

In summary, the control of the surface chemistry and the occurrence of clean surfaces allow the transformation of nanoparticles of isotropic shape into regular and often monodisperse nano-objects of anisotropic shape (cubes, rods, wires). It is possible that the inclusion of the initially present nanoparticles into super-lattices play an important role in these coalescence processes.

6. Organometallic approach to synthesis of metal oxide nanoparticles

Metal oxides display interesting electrical (semi-conductors, conducting glasses), optical and magnetic properties. These properties are associated to mechanical properties and absence of chemical evolution at moderate temperature which make them good candidates for many applications. Many efficient synthetic methods are known to produce high quality oxides (sol–gel, hydrothermal or solid-state syntheses). The organometallic method for synthesizing nanoparticles can also be extended to the preparation of oxides. It is conceivable either to synthesize first metal particles which may be oxidized in a second step, or to take profit of the high exothermicity of the oxidative decomposition of organometallics to prepare in one step oxide nano-objects of desired size and shape.

6.1. Oxidation of pre-formed metal nanoparticles

Decomposition of air and water sensitive organometallic precursors of oxophillic metals (zinc, indium, tin) in the presence of sub-stoichiometric amounts of water allows the synthesis of metal particles stabilized by an oxide shell. For example, in the case of tin, the growing oxide formed by the initial hydrolysis of the precursor $[Sn(NMe_2)_2]_2$ controls the growth of the metal particles which, at the end of the reaction display a tin core and a tin oxide shell (Fig. 9). These particles may further be entirely
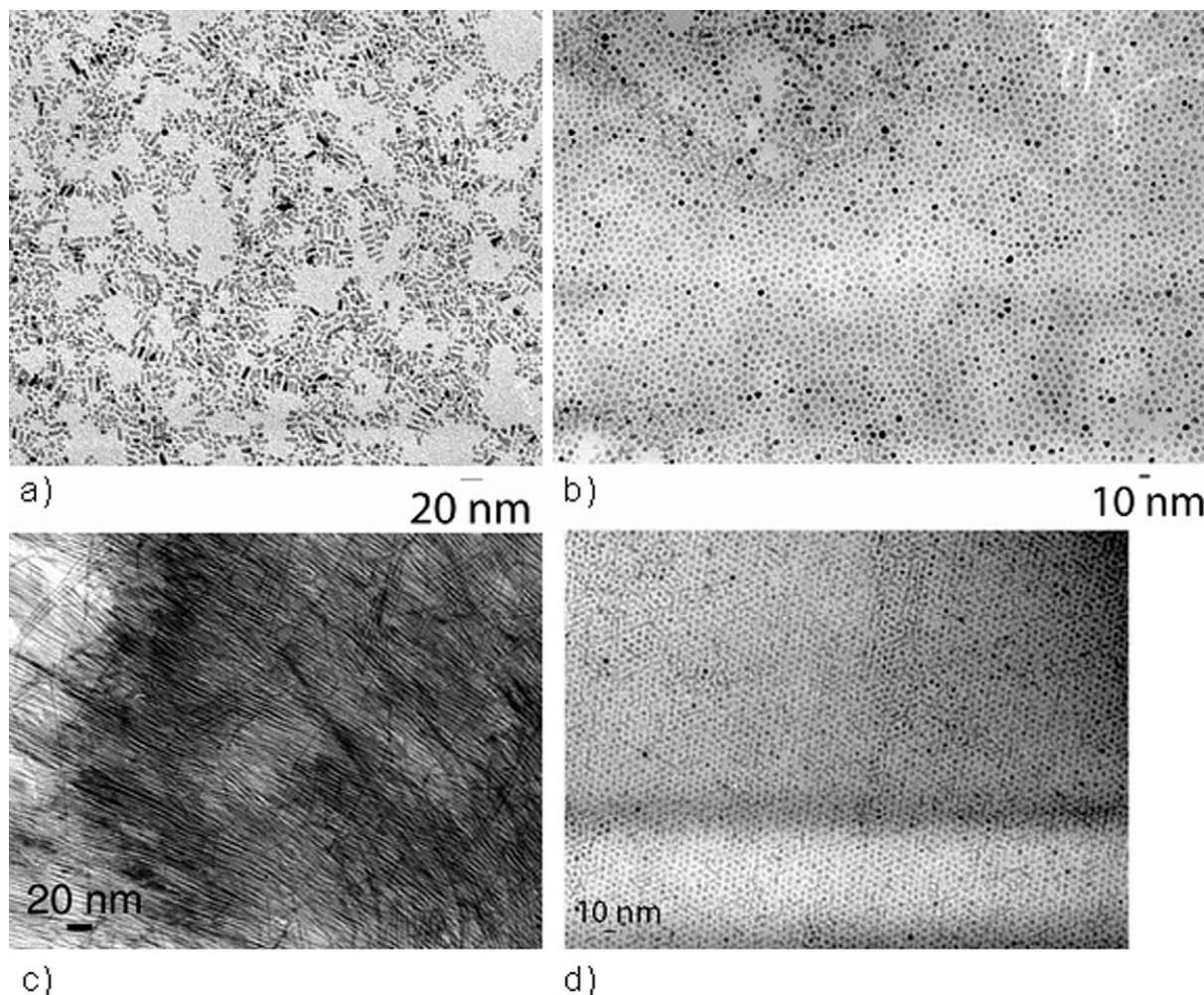
Fig. 10. Transmission electron micrographs of ZnO nanoparticles obtained in various experimental conditions: (a) nanorods, (b) spherical nanoparticles, (c) nanowires, (d) 2D self-organization of ZnO nanoparticles.

oxidized into SnO_2 without changes in their size or shape. This method was found appropriate for the deposition onto silicon of adhesive layers of nanoparticles (see here, below) [42].

6.2. Direct synthesis of metal oxide nanoparticles from organometallic precursors

A large number of organometallic compounds (i.e. $ZnCy_2$ or $InCp$; $Cy = C_6H_{11}$) react exothermally with air and water. If these compounds are initially dissolved into an organic solution in the absence of air and water and in the presence of long chain ligands (amines, carboxylic acids), the thermodynamic of the oxidation reaction remains the same and may lead the reaction to the formation of crystalline oxides but the kinetic can be slowed and allow a size and shape control of the particles. Thus the decomposition at room temperature of $ZnCy_2$ by ambient air or water vapour leads, in the presence of amines such as HDA, to spherical nanoparticles or nanorods according to the reaction conditions (Fig. 10) [43]. If the reaction is carried out in pure amine, nanowires, monodisperse in diameter, are obtained whereas in the presence of a mixture of ligands (amine + acid) fully monodisperse spherical particles form which self-organize into 2D or 3D super-lattices (Fig. 10) [44].

In summary, despite the large number of methods already available for the preparation of metal oxide nanoparticles, the new approach of organometallic preparation is interesting as it allows a good control of the particles growth and therefore, eventually, of their optical or electronic properties.

7. Interface with microelectronics and nanoelectronics

One of the most promising applications of nanoparticles concerns micro- or nanoelectronics, which raises the problem of the interface between the nanoparticles and silicon. In other terms, is it possible to integrate nanoparticles prepared in organic solutions into usual microelectronic devices? This problem was faced for the industrialization of gas sensors using as a sensitive layer SnO_2 nanoparticles as well as for preparing new nano-devices.

Gas sensors are based on the modulation of conductivity of semi-conducting oxides in the presence of gasses. The use of nanoparticles in such devices is advantageous since it allows an increase in selectivity, a better reproducibility and, quite unexpectedly, a resistance of the layer stable with time. The liquid phase deposition of a composite Sn/SnO_x or even $Sn/SnO_x/M$ ($M =$ doping metal: Pd, Pt, Ru) allows, in one step, the formation of an adhesive sensitive layer which is fully oxidized in situ on the chip using a polysilicon heater located on the back end of the device [45]. This cheap and practical approach allows the manufacturing of a new generation of gas sensors for automotive and domotic applications. The sensors are very sensitive as they can detect in air ca 1 ppm CO, 0.1 ppm ethylene and < 0.1 ppm NO_2. Other sensitive layers are presently used (In_2O_3) for the detection of oxidizing gasses [46].

In summary, nanoparticles prepared in organic solution may be integrated for the fabrication of microelectronic devices. They may also be the basis of novel nano-devices.

8. Conclusion

The classical methods of organometallic chemistry allow the control of the growth of species of nanometric size in solution. These objects are characterized by a very low size dispersity, an unoxidized surface and a surface coordination chemistry which may comprise hydrides, stabilizing ligands (amines, carboxylic acids, thiols) and, in some cases, directing ligands which will orientate their reactivity. The unoxidized surface allows the growth and coalescence of the particles to yield objects of controlled shape (spheres, cubes, rods, wires). Furthermore, the presence of surface ligands allows the organization of the particles in 2 or 3 dimensions (3D crystals of tin spheres, cubes of iron nanocubes, 2D crystals of cobalt nanorods, . . .). These nanoparticles display an interesting chemical reactivity in the field of catalysis together with adjustable physical properties. They can be integrated into present microelectronic devices and may be part of novel nano-electronic devices. This therefore should lead to a fast development of the use of 'organometallic nanoparticles' in the near future.

Acknowledgements

References

[1] A.F. Fourcroy, Système des connaissances chimiques et de leurs applications aux phénomènes de la nature et de l'art, Paris, Baudoin, An IX.
[2] M. Faraday, Philos. Trans. R. Soc. London 147 (1857) 145.
[3] Zsigmondy cité par A. Boutaric, Les colloïdes et l'état colloïdal, Félix Alcan, Paris, 1931.
[4] (a) M.P. Pileni, in: D.L. Feldheim, C.A. Foss Jr. (Eds.), Metal Nanoparticles, Marcel Dekker, New York, 2002, p. 207;
    (b) M.P. Pileni, Nat. Mater. 2 (2003) 145.
[5] Y. Lalatonne, L. Motte, V. Russier, A.T. Ngo, P. Bonville, M.P. Pileni, J. Phys. Chem. B 108 (2004) 1848, and references therein.
[6] (a) P. Toneguzzo, G. Viau, O. Acher, F. Fiévet-Vincent, F. Fiévet, Adv. Mater. 10 (1998) 1032;
    (b) G. Viau, R. Brayner, L. Poul, N. Chakroune, E. Lacaze, F. Fiévet-Vincent, F. Fiévet, Chem. Mater. 15 (2003) 486.
[7] G. Schmid, M. Bäumle, M. Geerkens, I. Heim, C. Osemann, T. Sawitowski, Chem. Soc. Rev. 28 (1999) 179.
[8] D.P. Dinega, M.G. Bawendi, Angew. Chem. Int. Edit. 38 (1999) 1788.
[9] S. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, Science 287 (2000) 1989.

[10] V.F. Puntes, D. Zanchet, C.K. Erdonmez, A.P. Alivisatos, J. Am. Chem. Soc. 124 (2002) 12874.

[11] S. Sabo-Etienne, B. Chaudret, Coordin. Chem. Rev. 178–180 (1998) 381.

[12] K. Philippot, B. Chaudret, in: D. Astruc (Ed.), Dendrimères et Nanosciences, C. R. Chimie 6 (2003) 1019.

[13] C. Pan, F. Dassenoy, M.J. Casanove, K. Philippot, C. Amiens, P. Lecante, A. Mosset, B. Chaudret, J. Phys. Chem. B 103 (1999) 10098.

[14] (a) A. Duteil, R. Quéau, B. Chaudret, R. Mazel, C. Roucau, J.S. Bradley, Chem. Mater. 5 (1993) 341;
(b) A. Rodriguez, C. Amiens, B. Chaudret, M.-J. Casanove, P. Lecante, J.S. Bradley, Chem. Mater. 8 (1996) 1978.

[15] (a) J. Osuna, D. de Caro, C. Amiens, B. Chaudret, E. Snoeck, M. Respaud, J.-M. Broto, A. Fert, J. Phys. Chem. 100 (1996) 14571;
(b) F. Dassenoy, M.-J. Casanove, P. Lecante, M. Verelst, E. Snoeck, A. Mosset, T. Ould Ely, C. Amiens, B. Chaudret, J. Chem. Phys. 112 (2000) 8137.

[16] J.S. Bradley, E.W. Hill, B. Chaudret, A. Duteil, Langmuir 11 (1995) 693.

[17] F. Dassenoy, M.-J. Casanove, P. Lecante, C. Pan, K. Philippot, B. Chaudret, Phys. Rev. B 63 (2001) 235407.

[18] (a) D. Zitoun, M. Respaud, M.-C. Fromen, M.-J. Casanove, P. Lecante, C. Amiens, B. Chaudret, Phys. Rev. Lett. 89 (2002) 37203;
(b) D. Zitoun, C. Amiens, B. Chaudret, M.-C. Fromen, P. Lecante, M.-J. Casanove, M. Respaud, J. Phys. Chem. B 107 (2003) 6997.

[19] K. Soulantica, A. Maisonnat, B. Chaudret, M.-C. Fromen, M.-J. Casanove, P. Lecante, Angew. Chem. Int. Edit. 40 (2001) 448.

[20] J.S. Bradley, E.W. Hill, S. Behal, C. Klein, B. Chaudret, A. Duteil, Chem. Mater. 4 (1992) 1234.

[21] M. Respaud, J.-M. Broto, H. Rakoto, A.R. Fert, L. Thomas, B. Barbara, M. Verelst, E. Snoeck, P. Lecante, A. Mosset, J. Osuna, T. Ould Ely, C. Amiens, B. Chaudret, Phys. Rev. B 57 (1998) 2925.

[22] I.M.L. Billas, A. Châtelain, W.A. de Heer, Science 265 (1994) 1682.

[23] O. Margeat, C. Amiens, B. Chaudret, M. Respaud, P. Lecante, unpublished results.

[24] N. Cordente, C. Amiens, B. Chaudret, M. Respaud, F. Senocq, M.-J. Casanove, J. Appl. Phys. 94 (2003) 6358.

[25] (a) O. Vidoni, K. Philippot, C. Amiens, B. Chaudret, O. Balmes, J.-O. Malm, J.-O. Bovin, F. Senocq, M.-J. Casanove, Angew. Chem. 38 (1999) 3736;
(b) K. Pelzer, O. Vidoni, K. Philippot, B. Chaudret, V. Collière, Adv. Funct. Mater. 13 (2003) 118.

[26] C. Pan, K. Pelzer, K. Philippot, B. Chaudret, F. Dassenoy, P. Lecante, M.-J. Casanove, J. Am. Chem. Soc. 123 (2001) 7584.

[27] F. Dassenoy, K. Philippot, T. Ould Ely, C. Amiens, P. Lecante, E. Snoeck, A. Mosset, M.-J. Casanove, B. Chaudret, New. J. Chem. 22 (1998) 703.

[28] T. Pery, K. Pelzer, J. Matthes, G. Buntkowsky, K. Philippot, H.-H. Limbach, Chaudret B., unpublished results.

[29] S. Jansat, M. Gómez, K. Philippot, G. Muller, E. Guiu, C. Claver, S. Castillón, B. Chaudret, J. Am. Chem. Soc. 126 (2004) 1592.

[30] S. Gomez, L. Erades, K. Philippot, B. Chaudret, V. Collière, O. Balmes, J.-O. Bovin, J. Chem. Soc. Chem. Comm. (2001) 1474.

[31] M. Gómez, K. Philippot, V. Collière, P. Lecante, G. Muller, B. Chaudret, New J. Chem 27 (2003) 114.

[32] F. Dumestre, S. Martinez, D. Zitoun, M.-C. Fromen, M.-J. Casanove, P. Lecante, M. Respaud, A. Serres, R.E. Benfield, C. Amiens, B. Chaudret, Faraday Discuss. Chem. Soc. 125 (2004) 265.

[33] K. Soulantica, A. Maisonnat, M.-C. Fromen, M.-J. Casanove, B. Chaudret, Angew. Chem. Int. Edit. 42 (2003) 1945.

[34] Y. Guari, C. Thieuleux, A. Mehdi, C. Reyé, R.J.P. Corriu, S. Gomez-Gallardo, K. Philippot, B. Chaudret, Chem. Mater. 15 (2003) 2017.

[35] Y. Guari, K. Soulantica, K. Philippot, C. Thieuleux, A. Mehdi, C. Reyé, B. Chaudret, R.J.P. Corriu, New J. Chem. 27 (2003) 1029.

[36] N. Cordente, C. Amiens, M. Respaud, F. Senocq, B. Chaudret, Nano Lett. 1 (2001) 565–568.

[37] K. Soulantica, A. Maisonnat, F. Senocq, M.-C. Fromen, M.-J. Casanove, B. Chaudret, Angew. Chem. Int. Edit. 40 (2001) 2983.

[38] F. Dumestre, B. Chaudret, C. Amiens, M.-C. Fromen, M.-J. Casanove, P. Renaud, P. Zurcher, Angew. Chem. Int. Edit. 41 (2002) 4286.

[39] F. Dumestre, B. Chaudret, C. Amiens, M. Respaud, P. Fejes, P. Renaud, P. Zurcher, Angew. Chem. Int. Edit. 42 (2003) 5213.

[40] E. Snoeck, R.E. Dunin-Borkowski, F. Dumestre, P. Renaud, C. Amiens, B. Chaudret, P. Zurcher, Appl. Phys. Lett. 82 (2003) 88.

[41] F. Dumestre, B. Chaudret, C. Amiens, P. Renaud, P. Fejes, Science 303 (2004) 821.

[42] (a) C. Nayral, T. Ould-Ely, A. Maisonnat, B. Chaudret, P. Fau, L. Lescouzères, A. Peyre-Lavigne, Adv. Mater. 11 (1999) 61;
(b) C. Nayral, E. Viala, P. Fau, F. Senocq, J.-C. Jumas, A. Maisonnat, B. Chaudret, Chem.-Eur. J. 6 (2000) 4082.

[43] M. Monge, M.L. Kahn, A. Maisonnat, B. Chaudret, Angew. Chem. Int. Edit. 42 (2003) 5321.

[44] M.L. Kahn, M. Monge, E. Snoeck, A. Maisonnat, B. Chaudret, Small, in press.

[45] P. Fau, M. Sauvan, S. Trautweiler, C. Nayral, L. Erades, A. Maisonnat, B. Chaudret, Sensor. Actuat. B – Chem. 78 (2001) 83.

[46] (a) K. Soulantica, L. Erades, M. Sauvan, F. Senocq, A. Maisonnat, B. Chaudret, Adv. Funct. Mater. 13 (2003) 553;
(b) P. Menini, F. Parret, M. Guerrero, A. Martinez, K. Soulantica, L. Erades, A. Maisonnat, B. Chaudret, Sensor. Actuat. B – Chem. (2004) in press.