Tin Superstructures

Spontaneous Formation of Ordered 3D Superlattices of Nanocrystals from Polydisperse Colloidal Solutions**

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The synthesis and ordering of nanocrystals into nanocrystal superlattices (NCSs) is timely and of prime importance for applications involving physical properties.[1] The formation of NCSs requires the presence of ligands for controlling the size, shape, and monodispersity of the particles[2,3] and for favoring their self-assembly. This process generally results from the evaporation of solvent[4,5] from a solution of the nanoparticles or precipitation of particles by the addition of a non-solvent.[6,7] It requires strictly monodisperse nanocrystals that result from specific synthetic routes[8] or tedious size-selection processes.[2,5–7] Considerable effort has recently been devoted to the formation of crystalline superlattices of metals,[4,5b,8d,9,10] metal alloys,[1d,7] metal oxides,[8a–c,11,12] sulfides,[5] and semiconductors.[6] The superlattices that have been characterized generally adopt a compact fcc or hcp structure.[4–7,10–13] A few examples of NCSs display orientational order between the nanocrystals.[4,10] Molecular dynamic

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simulations have, however, predicted that monodisperse nanocrystals stabilized by long-chain ligands could crystallize into noncompact superstructures in which the crystallographic axes of the individual nanocrystals would be aligned.[14] Structures of this type have been detected but remain very rare.[15]

We have previously shown that a range of ligands, from water to long-chain amines, are able to control the growth of nanoparticles that are prepared by decomposition of an organometallic precursor, and even to allow self-assembly of monodisperse particles into 2D and 3D superstructures.[16] However, recent results[1d,17,18] emphasize the importance of the presence of two types of ligands/surfactants for achieving simultaneously the control of monodispersity, self-assembly, and, in some cases, the shape of the particles. In these cases, however, a reaction between the different ligands may proceed under the reaction conditions, which renders the rationalization of the observations difficult. We report here an alternative system based on the association of an acid with its conjugated base, namely an ammonium/amine system, which should produce a less or nonevolutive reaction medium. This system leads to the spontaneous formation of 3D superlattices containing monodisperse tin nanocrystals exhibiting translational and orientational order. These NCSs are grown directly from a solution containing polydisperse tin particles.

UV irradiation (365 nm) of $[\{Sn(NMe_2)_2\}_2]$[19] in toluene at room temperature in the absence of stirring and in the presence of one equivalent of hexadecylamine (HDA) leads to the formation of large square-shaped particles which display a broad size distribution centred near 50 nm (TEM analysis). They are isolated or agglomerated, but without any sign of order, and consist of pure tetragonal tin (XRD evidence). A spectacular change is observed in the reaction products when the same reaction conditions is used, but with a mixture of HDA and its HCl adduct (HDA·HCl) at various relative concentrations in place of pure HDA. Different types of superstructures are produced which may coexist in the same preparation (Figure 1): 1) three-dimensional crystalline networks (nanocrystal superlattices (NCS **1**)) consisting of monodisperse tin particles with dimensions of about 18 × 15 nm (Figure 1a); 2) a second type of crystalline arrangement (NCS **2**) accommodating monodisperse larger and more anisotropic particles (Figure 1b); 3) particles showing some size polydispersity which appear either isolated, assembled into disordered superstructures, or, in some cases, assembled into monolayers displaying a mosaic-like pattern (Figure 1c). In contrast to recent results obtained with indium,[16] the thickness of the NCSs on the microscopy grids, the polydispersity of the particles in solution, and the absence of monolayers suggest that self-organization of the nanocrystals does not occur on the microscopy grid. The structure of the NCSs has been studied by HREM and electron diffraction at different tilting angles of the support. From a morphological viewpoint, the network NCS **1** appears as a single supercrystal of particles with at least two well-defined edges. The Sn particles are all identical in size and morphology and display a slightly elongated shape (aspect ratio ca. 1.2:1, long axis: 18 nm, short axis: 15 nm, interparticle distance: ca. 3 nm). They display the tetragonal structure of Sn and

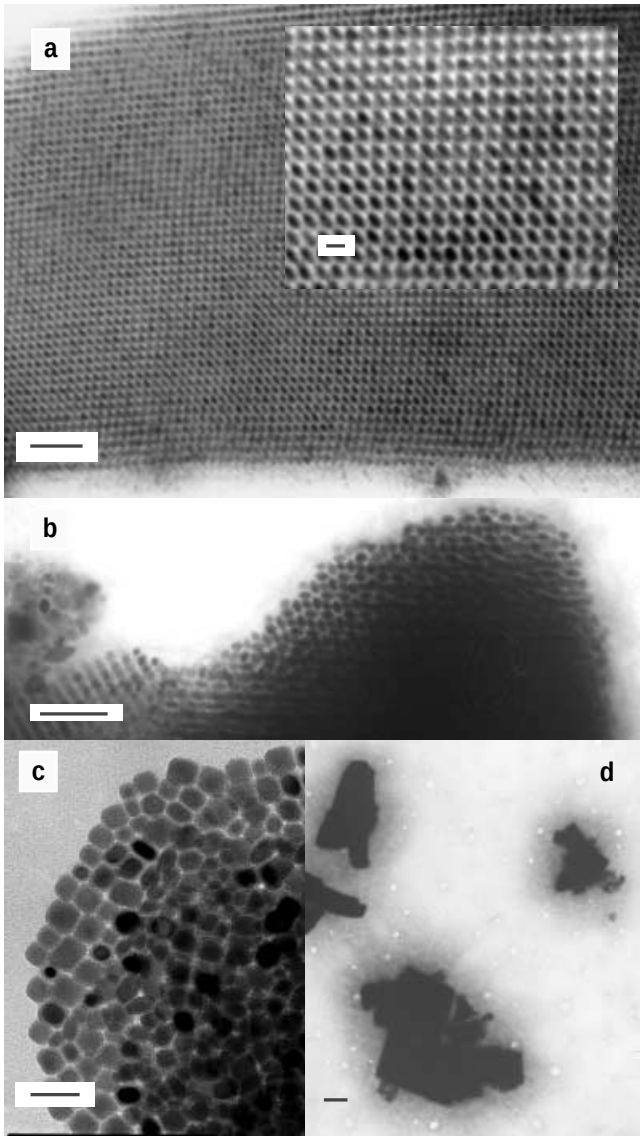

Figure 1. Different objects present in the colloidal solution. a) NCS **1** network (scale bar: 100 nm). Inset: higher magnification (scale bar: 20 nm); b) NCS **2** network (scale bar: 100 nm); c) unorganized material outside the NCSs (scale bar: 50 nm); d) general view of the sample (scale bar: 1 μm).

are oriented in nearly the same direction (Figure 2b). A slight misalignment, which never exceeds 15°, is observed in HRTEM images and revealed by a Fourier Transform diffractogram of the image, as well as by the high-angle electron diffraction spots of the tin network measured on one NCS (Figure 2c). This observation demonstrates that the NCSs are characterized not only by a translational but also by an orientational symmetry. The structure of the superlattice is not compact, but probably monoclinic ($a = 15.6$, $b = 16$ nm; $\alpha = \beta = 90$, $\gamma = 77°$), although the presence of some lattice distortion in the thinner areas prevents a full identification (Figure 2a).

The second superstructure, NCS **2**, displays a surprisingly complex pattern (Figure 3). The individual particles display an elongated shape (25 nm long and aspect ratio ca. 1.6:1).

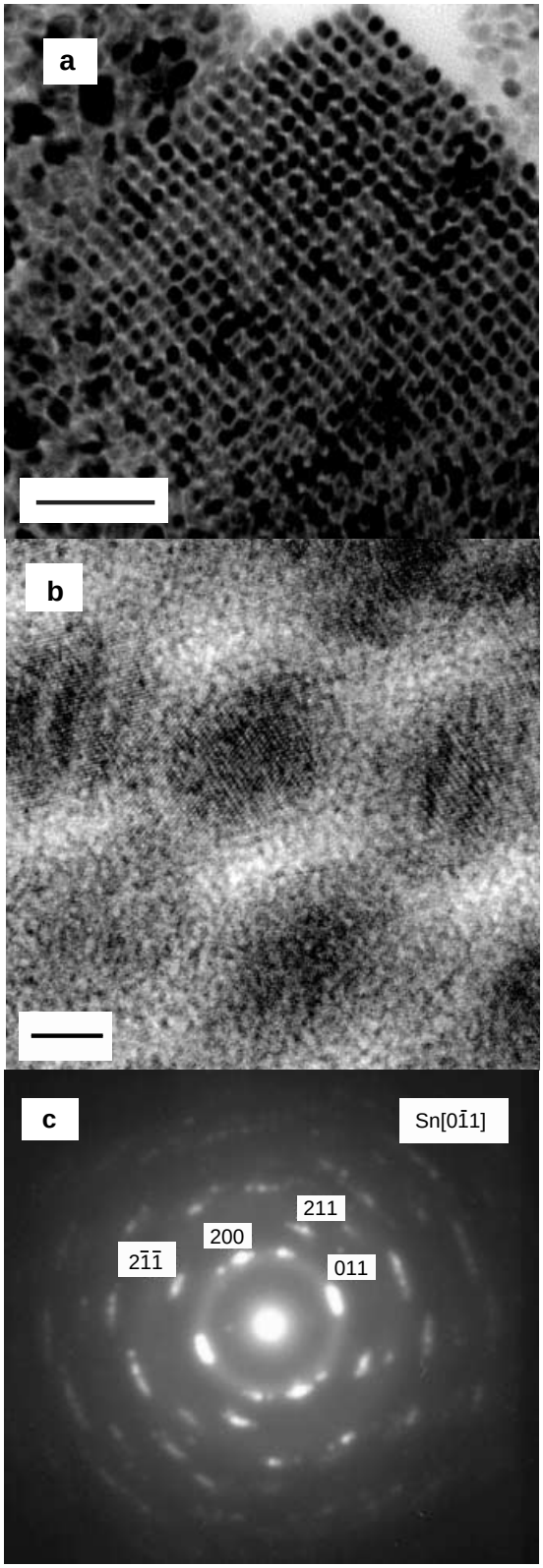

Figure 2. NCS **1** network. a) View of a faceted superlattice. Some disordered material may be observed next to the crystal (scale bar: 100 nm); b) HREM image illustrating the alignment of the atomic planes of individual particles (scale bar: 5 nm); c) electron diffraction image of a part of NCS **1** network showing the tin β structure and demonstrating the crystallographic alignment of the particles with a maximum deviation of 15°.

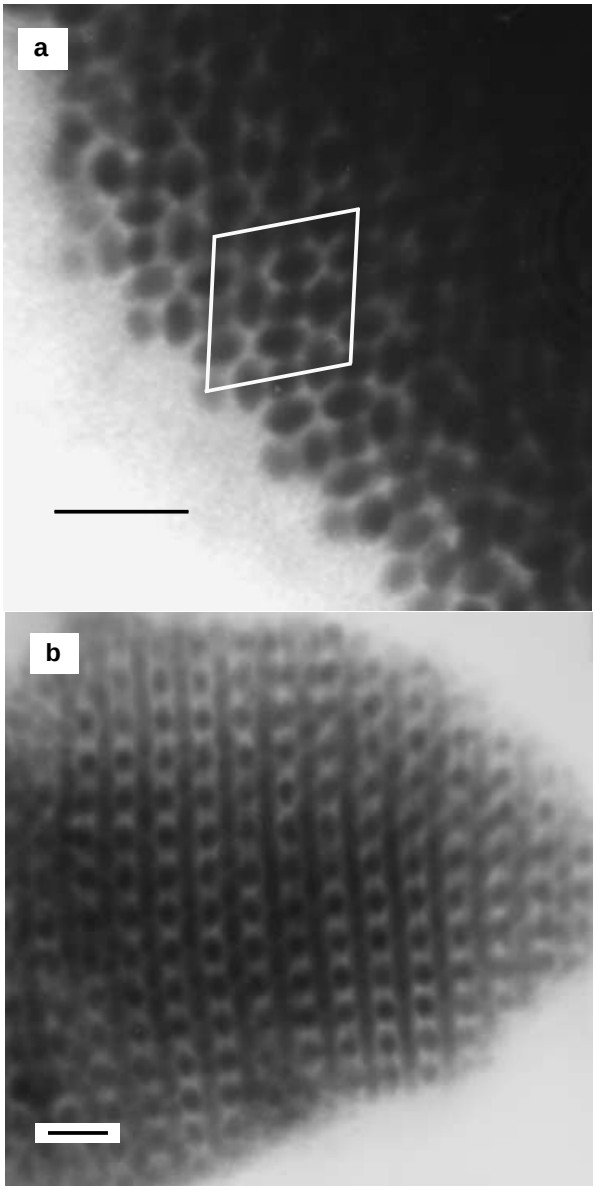

Figure 3. NCS **2** network. a) Superlattice of "crosses" where the supercell unit is indicated in the white box (scale bar: 50 nm); b) another view of a NCS **2**. The different angle allows another pattern to appear (scale bar: 50 nm).

The smaller recognizable pattern in the thin regions is a cruciform arrangement of four particles surrounding a single smaller particle that is, in our opinion, an identical particle oriented perpendicular to the other four. These crosses are organized into rows with their axes alternately rotated by a small positive or negative angle from the mean direction of the super-lattice. The projected supercell unit is larger than one cross and is depicted in Figure 3a. Different orientations demonstrate the complexity of the structure, which is not consistent with the presence of simple lattices (such as fcc, hcp, and bcc). To the best of our knowledge this is the first example of such an elaborate structure of NCS. Up to now only regular "side-by-side" arrangements of nanoparticles have been encountered.

This complicated process involves both a crystallization and a size adjustment of the particles. We studied the influence of several reaction parameters to gain some knowledge of the formation of these objects. We found that the concentration of the reagents, the use of $[\{Sn(NMe_2)Cl\}_2]$[20] as the chloride source, the addition of free $HNMe_2$, the nature of the solvent and the presence of water in it, as well as the reaction time are some of the parameters that determine the outcome of the crystallization. Conditions have thus been identified which favor the production of NCS **1** almost exclusively, and other conditions where both NCSs were produced (see Experimental Section). We also found that the formation of NCSs does not proceed in THF or if the toluene reaction solution is stirred. In the latter case, a high degree of size polydispersity and almost no organization are observed. Finally, the reaction and organization proceed using dodecylamine (DDA) in place of HDA and with similar constraints on concentration, but not when octylamine was used.

A rational for these observations can be proposed. In the absence of stirring, a gradient of metal and ligand concentrations may form between the layers directly exposed to UV light and the inner parts of the solution, thus accounting for the presence of particles of different sizes and shapes in the reaction mixture. The particles formed may also fluctuate in size and shape in solution as previously observed.[21] Some particles of a given size and ligand environment may self-assemble into NCSs in solution as a result of size-dependent, attractive interparticle forces.[22] While growing, the resulting NCSs will precipitate in toluene but may continue to incorporate adequate particles present in the liquid phase. The continuous formation of particles of size appropriate for inclusion into the growing NCS results from size re-equilibration in solution. It is noteworthy that this process does not operate in a polar solvent, such as THF, which may firmly bind to the tin surface and hence may prevent re-equilibration. The presence of two types of networks results from the necessity to accommodate particles of different shapes and may be related to the concentration of chloride ions.

In conclusion, we have reported the synthesis of identical tin nanoparticles included into tin superstructures of micron sizes. The particles display uniform size and crystallographic orientation. The noncompact nature of the superlattices points towards a crystallization of both the particles and their ligand shells, as for molecular species. The formation of the NCSs results from 1) fractional crystallization in solution, a long-known process that enables the spontaneous size selection of particles, and 2) size fluctuation that affords new particles to be incorporated into the NCSs. This in turn allows the control in one step of the shape, monodispersity, and ligand environment of the particles. This complex process has, to the best of our knowledge, no precedent. Further work, currently in progress, will be necessary to elucidate the mechanism of growth of these NCSs and the generality of this approach.

Experimental Section

All noncommercial compounds were prepared under argon by using standard Schlenck techniques. A glove-box was used for the preparation of the starting solutions. The solvents used were distilled under sodium and degassed through three freeze-pump-thaw cycles. The long-chain amines were purchased from Fluka. The hydrochloric salts were prepared by addition of an excess of a 2 M solution of HCl in diethyl ether to a solution of the corresponding amine in toluene. The precipitate which formed immediately was stirred for 2 h, then washed with toluene. Complete evaporation of the solvent gave the hydrochloride salt.

$[\{Sn(NMe_2)Cl\}_2]$ was prepared in a similar way to $[\{Sn(NMe_2)_2\}_2]$ but by adding only one equivalent of $LiNMe_2$ to $SnCl_2$, and was isolated by sublimation at 110 °C. The product was characterized by X-ray crystal-structure analysis (not reported here); ^{1}H NMR: $\delta =$ 2.32 ppm ($^3J_{Sn\text{-}H} = 26.7$ Hz).

Typical procedures leading to NCS **1**: A solution of $[\{Sn(NMe_2)_2\}_2]$ (51.7 mg, 0.250 mmol of Sn) in freshly distilled and degassed toluene (the distilled toluene contains about 50 ppm of H_2O) was added to a suspension of a mixture of HDA·HCl (26.1 mg, 0.094 mmol) and HDA (8.5 mg, 0.035 mmol) in the same solvent. The total volume was adjusted to 5.5 mL. Alternatively, a mixture of $[\{Sn(NMe_2)_2\}_2]/[\{Sn(NMe_2)Cl\}_2]$ (36.7 mg, 0.177 mmol/14.5 mg, 0.073 mmol) could be used. In this case HDA was the only amine used and the two Sn precursors left to react for a few minutes before adding the reaction mixture to HDA (30.2 mg, 0.125 mmol). The total amount of toluene used ws 5.5 mL. Monitoring of the reaction between $[\{SnCl(NMe_2)_2\}]$ and $[\{Sn(NMe_2)_2\}_2]$ by ^{1}H NMR spectroscopy showed that a tin complex identified as $[\{Sn_2Cl(NMe_2)_3\}]$ is formed. The latter complex was detected as one of the products of the reaction of HDA·HCl with $[\{SnCl(NMe_2)\}_2]$. In both cases, the resulting clear yellow solution was stirred and then left standing for 1 h before exposure to UV light for 30 h and 46 h, respectively, without stirring. The whole cell was then transferred into the glove-box and a drop of the crude suspension obtained after removing the majority of the clear yellow supernatant was placed on a TEM grid and dried. The product for XRD measurements was isolated by simple removal of the supernatant solution and drying. All efforts to wash the powder resulted in loss of organization.

Typical procedure leading to NCS **1** and NSC **2**: The same general procedure was used starting from a mixture of $[\{SnCl(NMe_2)\}_2]$ (7.9 mg, 0.040 mmol in Sn) and $[\{Sn(NMe_2)_2\}_2]$ (42.5 mg, 0.210 mmol in Sn). The two compounds were reacted for 30 min in toluene (3 mL) and then a solution of HDA (30.2 mg, 0.125 mmol) in toluene (2.5 mL) was added. The clear yellow solution was left without stirring under UV light for 48 h and characterized as described above.

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