

Organization of nanoparticles

Spontaneous Formation of Ordered 2D and 3D Superlattices of ZnO Nanocrystals**

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A large amount of research is presently devoted to the synthesis of nanoparticles of zinc oxide.^[1–11] Zinc oxide is a luminescent, wide-bandgap semiconductor material that may find applications in a wide range of domains.^[12] However, many applications require the organization of the nanoparticles into two- or three-dimensional (2D or 3D) superlattices.^[12] Recently, Yang and co-workers reported a 2D organization of nanorods that display lasing properties in the ultraviolet region.^[13] This very efficient organization was obtained by a physical method, but chemical approaches towards such organizations would also be of interest since they are easy to perform and allow for a facile scale-up procedure. In this respect, we recently reported a very simple synthetic method for the preparation of well-defined crystalline zinc oxide nanoparticles.^[14] The process takes advantage on one hand of the very exothermic reaction of the organometallic precursor bis(cyclohexyl) zinc (**1**) with water to produce crystalline zinc oxide and, on the other hand, of the kinetic control of the decomposition by using long-alkyl-chain amine ligands. However, if the use of amine ligands allows access to ZnO nanoparticles of low size dispersity,

these particles are not monodisperse and consequently, no 2D or 3D organizations were observed.

A lot of effort has recently concerned the formation of crystalline 2D or 3D superlattices of metals,^[15–20] alloys,^[21–23] or metal oxides.^[24–26] In this field, we recently reported the formation of superlattices of tin nanoparticles^[27] or iron nanocubes^[28] using a combination of two types of ligands. In these two examples, the nanocrystal superlattices result from a crystallization process in solution involving both the particles and their ligand shells. This phenomenon has proven to be efficient for different zero-valent metallic nanoparticles. For metal-oxide nanoparticles, a few 3D organizations resulting from particle self-assembly on a surface have been described.^[24–26] The ZnO nanoparticles we recently reported^[14] are produced by evaporating the solvent of the reaction solution, a method used in molecular chemistry to form monocrystals. Providing we could produce monodisperse particles, a similar method seemed attractive to form 2D and 3D ordered superlattices. We report here the synthesis of ZnO nanoparticles stabilized by a combination of amine and acid ligands and their spontaneous organization into 2D- and 3D ordered superlattices from colloidal solutions.

The synthesis of the ZnO nanoparticles is carried out by slow hydrolysis in air of a THF solution containing the precursor ZnCy₂ (**1**) as well as one equivalent of a long-alkyl-chain amine and half an equivalent of a long-alkyl-chain acid. Thus, when the reaction mixture was exposed to air and left standing at room temperature, the solvent slowly evaporated and left a white and luminescent product, which was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) as crystalline, isotropic ZnO nanoparticles (≈ 3.5 nm mean diameter) and very low size dispersity. This procedure was adapted from that previously described elsewhere.^[14] Different ligand systems were studied, combining hexadecylamine, dodecylamine, and octylamine on one side (HDA, DDA, and OA) and octanoic acid, oleic acid, and lauric acid on the other (OcA, OIA, and LcA). Table 1 summarizes the results obtained under various reaction conditions and Figure 1 illustrates some examples of the materials obtained. All new materials were characterized by TEM as well as by XRD and/or selected-area electron diffraction (SAED). In all cases the nanoparticles were of isotropic shape and consistently displayed the hexagonal zincite phase (space group $P6_3mc$). It is noteworthy that the presence of a carboxylic acid is essential to obtain monodisperse isotropic nanoparticles but that the nature of the amine and acid ligands has only a very limited influence on the size of the particles.

If the synthesis is carried out in similar conditions but in the absence of solvent, a liquid fraction is formed even if the reagents are initially solids. Whatever the proportions of the components, the reaction yields isotropic nanoparticles, in contrast to the long nanorods obtained when only long-alkyl-chain amines are present,^[14] which is probably a result of modification of the self-organization of the ligands. The size of the particles obtained under these conditions is independent of the reaction conditions and similar to those resulting from the reaction in THF, but with a broader disper-

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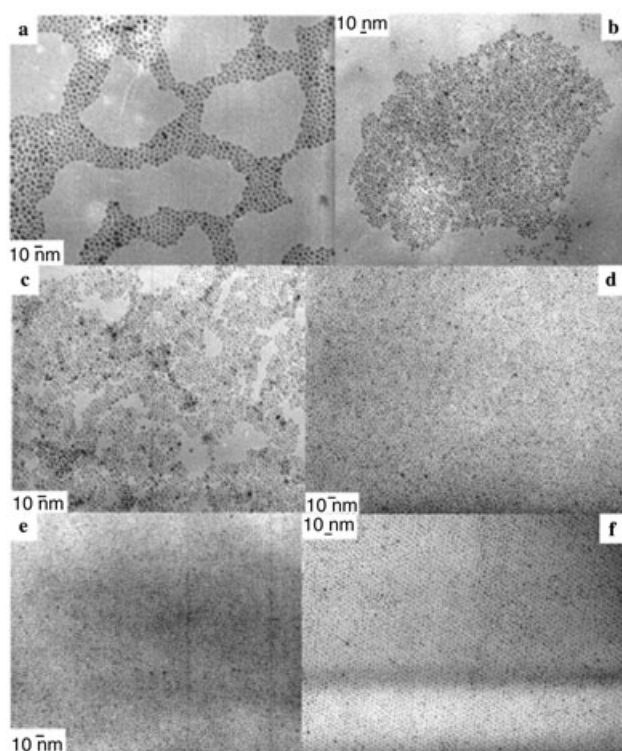


Figure 1. TEM pictures of ZnO nanoparticles obtained in the presence of: a) OA and OIA (1:1) without other solvent; b) OA and OIA (2:1) without other solvent; c) OA and OIA (10:1) without other solvent; d) OA and LcA (1:1) in THF; e) DDA and OcA (1:1) in THF; f) HDA and OIA (1:1) in THF.

sity. This explains therefore why 2D or 3D organizations have been previously obtained only with nanoparticles synthesized in THF.

All ZnO nanoparticles are fully soluble in common organic solvents, which leads to clear and luminescent solutions. 2D organizations were spontaneously obtained by depositing one drop of the colloidal solution onto a carbon-coated copper grid. A TEM micrograph displays the pres-



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Bruno Chaudret graduated from the Ecole Nationale Supérieure de Chimie de Paris in 1975. He received his PhD from Imperial College (London) in 1977 with Prof. G. Wilkinson and his "Doctorat d'Etat" in 1979 from Université Paul Sabatier (Toulouse, France) with Prof. R. Poilblanc. He is presently *Directeur de Recherche* and leader of the group "Nanostructures and Organometallic Chemistry" in the *Laboratoire de Chimie de Coordination CNRS* in

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Table 1. Summary of the results obtained under various reaction conditions.^[a]

Ligand ^[b] (per mole ZnCy ₂)	Solvent	Nanosphere size [nm] ^[c]
HDA/0.5 OcA	THF	3.5 ± 1.0
HDA/0.5 OIA	THF	3.1 ± 1.1
HDA/0.5 LcA	THF	2.8 ± 0.8
DDA/0.5 OcA	THF	3.5 ± 0.9
DDA/0.5 OIA	THF	3.5 ± 1.7
DDA/0.5 LcA	THF	3.5 ± 1.0
OA/0.5 OcA	THF	3.1 ± 0.9
OA/0.5 OIA	THF	3.7 ± 0.9
OA/0.5 LcA	THF	3.2 ± 0.7
OA/0.5 OcA		3.6 ± 1.1
OA/0.5 OIA		3.8 ± 1.8
OA/0.5 LcA		3.7 ± 1.4
2 OA/0.5 OIA		3.6 ± 1.4
5 OA/0.5 OIA		3.4 ± 1.5
2 OA/OIA		3.6 ± 1.3

[a] All procedures were carried out at room temperature, with an incubation time of 17 hours. The particles then were maintained in moist air for 4 days. For each experiment, the concentration of the zinc precursor was 0.042 M. [b] HDA, DDA, OA, OcA, OIA, and LcA stand for hexadecylamine, dodecylamine, octylamine, octanoic acid, oleic acid, and lauric acid, respectively. [c] The mean diameter of the obtained nanospheres was evaluated by fitting of the histogram with a Gaussian curve. The first value corresponds to the centre of the peak whereas the second one corresponds to two times the standard deviation of the Gaussian distribution, or approximately 0.849 times the width of the peak at half height.

ence of monolayers of well-organized monodispersed nanoparticles (Figure 1 d, e, and f). In order to investigate the morphology, size, and organization of the ZnO particles, a specific TEM experiment was performed on a CM20 STEM-Field Emission Gun (FEG) microscope. Figure 2 a shows a low-magnification TEM micrograph of a monolayer of ZnO nanoparticles prepared using HDA and OIA and its Fourier transform (FT, inset). The spots in the FT and the sixfold symmetry of the pattern demonstrate the regular hexagonal arrangement of the ZnO nanoparticles in the monolayer. Thanks to the high coherence of the FEG electron beam, Bragg spots located very close to the central beam can be resolved by electron diffraction experiments. Figure 2 b shows a SAED pattern of the monolayer over an area of a few tens of micrometers. In this figure, the reflections can be observed around the transmitted beam on a circle, the diffraction vectors of which are characteristic of the periodicity of the monolayer, that is, they correspond to the mean distance between the ZnO particles. Evaluation of these diffraction vectors leads to a period of 7.8 nm. The most intense reflections reproduce the sixfold symmetry of the particle organization with a dispersion of about 13°. This SAED experiment confirms the high quality of the hexagonal 2D arrangement of the ZnO particles over very large areas.

3D superlattices were obtained through slow evaporation of colloidal THF solutions. The superlattices are not monodisperse in size but display uniform hexagonal shapes. Interestingly, this shape may be related to the intrinsic hexagonal crystallographic structure of ZnO, as previously observed for the organization of iron nanocubes.^[27,28] Figure 3

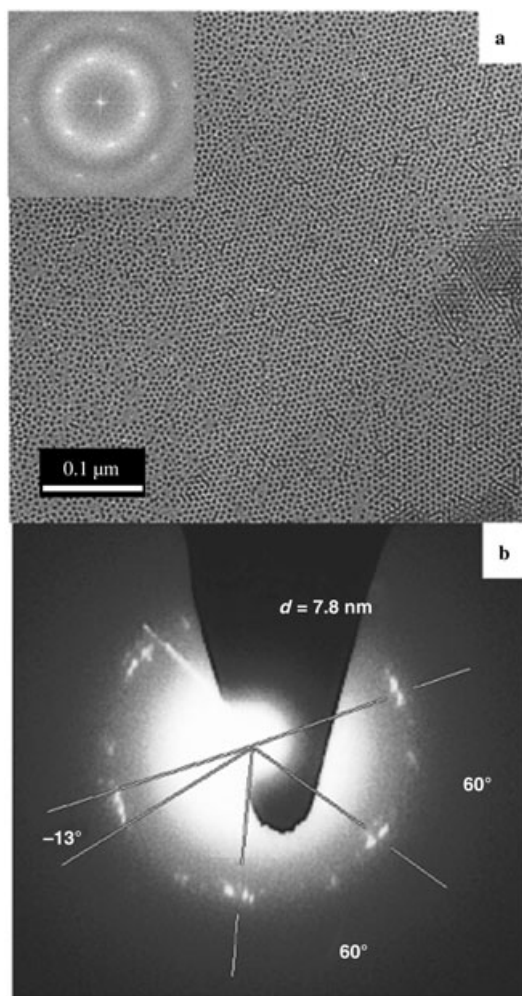


Figure 2. a) 2D assembly of ZnO nanoparticles (inset: corresponding Fourier transform); b) SAED pattern of the monolayer over an area of few tens of micrometers.

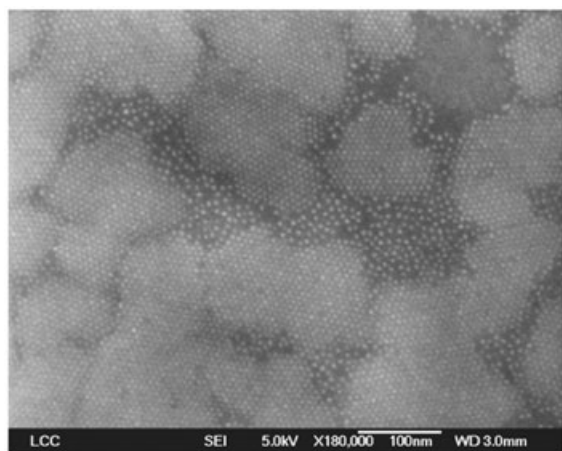


Figure 3. SEM-FEG image of 3D superlattices of ZnO nanoparticles prepared in the presence of HDA and OIA.

shows SEM-FEG pictures of small 3D superlattices of 3.1-nm ZnO nanoparticles obtained from HDA and OIA. Larger 3D superlattices may be obtained when crystallization is performed until the quasi-complete evaporation of the solvent. Figure 4 shows 3D superlattices of around

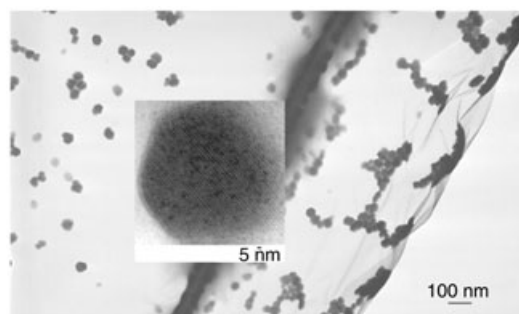


Figure 4. TEM images of 3D superlattices of ZnO nanoparticles prepared in the presence of HDA and LcA; inset: high-resolution image of one superlattice.

50 nm composed of 2.8-nm ZnO nanoparticles prepared using HDA and LcA as ligands. It has to be emphasized that, in this case, the formation of the 3D superlattices proceeds as for crystallization of molecular species: the supercrystals appear in the crystallization solution when the concentration of nanoparticles increases due to solvent evaporation. The TEM grid is then prepared by depositing a drop of the crystallization solution containing the superlattices in suspension into the solvent. Redissolution of these superlattices leads to colloidal solutions, which can be deposited again as 2D or 3D superlattices. The key point of the achievement of these 2D or 3D organizations seems to be the presence of both acids and amines in the reactive medium. Acid ligands may, on one hand, coordinate strongly to the zinc oxide particles, hence promoting monodispersity and preventing further changes in size and shape in contrast to syntheses carried out in the presence of only amine ligands. On the other hand, the transfer of protons to amines may lead to charged ligands (ammonium and carboxylate), which will promote the formation of the organizations.

In conclusion, we describe in this paper the high-yield synthesis of monodisperse and crystalline ZnO nanoparticles of ≈ 3.5 nm mean size, which are stabilized by a combination of long-chain carboxylic acid and amine ligands. These particles spontaneously organize into 2D and 3D superlattices through a very simple chemical route inspired by molecular crystallization.

Keywords:

2D organization • 3D organization • colloids • oxides • self-assembly

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