Zinc Oxide Nanoparticles

Room-Temperature Organometallic Synthesis of Soluble and Crystalline ZnO Nanoparticles of Controlled Size and Shape

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ZnO is a wide-band-gap semiconductor (3.37 eV) that displays interesting luminescent properties, which include the recent demonstration of ultraviolet lasing from nanowires.[1,2] These properties have stimulated the search for new synthetic methodologies for well-controlled ZnO nanostructures. Several reports on high-temperature physical[3,4] or chemical[5–9] ZnO syntheses have recently been published. The chemical methods appear to be of particular interest since they offer the potential of facile scale-up, and occur at moderate temperatures (100–200 °C). The synthesis is generally carried out in water or alcohols using zinc salts as starting materials in the presence of a base.[5–7] These methods are convenient and may lead to nanomaterials of controlled morphology. However, the synthesis makes use of ionic species, which may react with the growing oxide and modify the properties of the final material, whether chemical or physical. An alternative method using the organometallic complex $[Zn(C_2H_5)_2]$ (**1**) as a precursor was reported by Klabunde et al.[8] However, it involves the transformation of **1** into an alkoxide prior to hydrolysis and heat treatment. Complex **1** was also recently used for the synthesis of ZnO[9] following a "high-temperature organometallic method" derived from that originally reported by Bawendi et al.[10] in the presence of ligands, such as tri-*n*-octyl phosphane oxide (TOPO) and amines.

In separate studies, we have evidenced the interest of organometallic complexes for the preparation of metal nanoparticles of controlled size and shape.[11–15] This methodology was extended to the synthesis of metal oxide nanoparticles through a two-step approach : 1) the formation of metal nanoparticles through decomposition of the organometallic precursor, and 2) the oxidation of the as-formed nanoparticles.[16–18] This approach has allowed the preparation of SnO_2 and In_2O_3 particles for gas sensing[16,17] and was also used for the preparation of ZnO particles from the bisalkyl zinc precursor $[Zn(c\text{-}C_6H_{11})_2]$ (**2**).[18] However, we reasoned that most organometallic complexes are air-sensitive and decompose exothermically in air. A controlled oxidation of the precursor in solution could therefore lead in one step to oxidized nanomaterials (oxides or hydroxides), the shape and size of which could in principle be controlled by the ligands or surfactants present.

Herein we report the *room-temperature* synthesis of ZnO nanoparticles of controlled size and shape in solution. This route provides crystalline nanoparticles of regular disk or rod shapes depending on the characteristics of the solution, in terms of solvent, ligand, and concentration. The oxide particles are fully soluble in organic solvents giving rise to clear and luminescent solutions from which regular monolayers can be deposited.[19]

When a solution of the dicyclohexylzinc(II) compound **2** in THF[20] is left standing at room temperature in open air, the solvent slowly evaporates and leaves a white luminescent residue, which was characterized by XRD and TEM as being agglomerated nanoparticles of ZnO with a zincite structure that display no defined size or shape. If, however, ligands such as long chain amines are added under argon to a solution of **2** in THF, and the resulting mixture is treated as before, well-defined nano-objects are formed, the size and shape of which depend upon the reaction conditions. For example, the reaction can be carried out in THF using hexadecylamine (HDA) as a ligand. After a reaction time of 17 h and evaporation of the solvent (concentration of reagents: $0.042\ mol\,L^{-1}$; standard procedure[21]), homogeneous nanorods of approximately 8.1×2.6 nm are obtained, which can be redissolved in THF (Figure 1a). Several parameters were identified as important for controlling the size, shape, and homogeneity of the nanomaterials, namely the nature of the ligand, the relative concentration of the reagents, the solvent, the overall concentration of the reagents, the reaction time, the evaporation time, and the reaction/evaporation temperature. These parameters and their influence on the ZnO nano-objects produced are listed in Table 1 and, in some cases, illustrated in Figures 1 and 2.[21] All new materials were characterized by X-ray diffraction (XRD) and/or selected-area electron diffraction (SAED) and consistently display the same pattern. The XRD pattern corresponds to the hexagonal zincite phase, space group $P6_3mc$ (see Supporting Information; S1).

It is evident from Table 1 that the control of the size and morphology of the ZnO particles results from the nature of the solution (solvent, ligands, concentrations, and so on). We have previously shown, in particular by NMR spectroscopy, that the shape control of metal nanoparticles was related to ligand coordination.[13] A similar effect seemed however very surprising in the case of oxides and led us to undertake an NMR study. The addition of HDA to **2** in $[D_8]$THF leads to ^1H and $^{13}C\{^1H\}$ NMR spectra that suggest the coordination of the amine to **2** through nitrogen atoms. After oxidation, the $^{13}C\{^1H\}$ NMR spectra of the reaction mixture do not reveal the presence of any trace of **2** but show peaks attributed to HDA. The signals corresponding to the carbon atoms in the α, β, and γ positions relative to nitrogen at $\delta = 42.69$, 34.58, and 27.31 ppm, respectively, are very broad (see Figure 3). This phenomenon has been observed previously on ruthenium nanoparticles[13] and can be attributed to a fast exchange between free ligand molecules in solution and coordinated ligand molecules linked to ZnO through nitrogen atoms. This therefore demonstrates that throughout the process of

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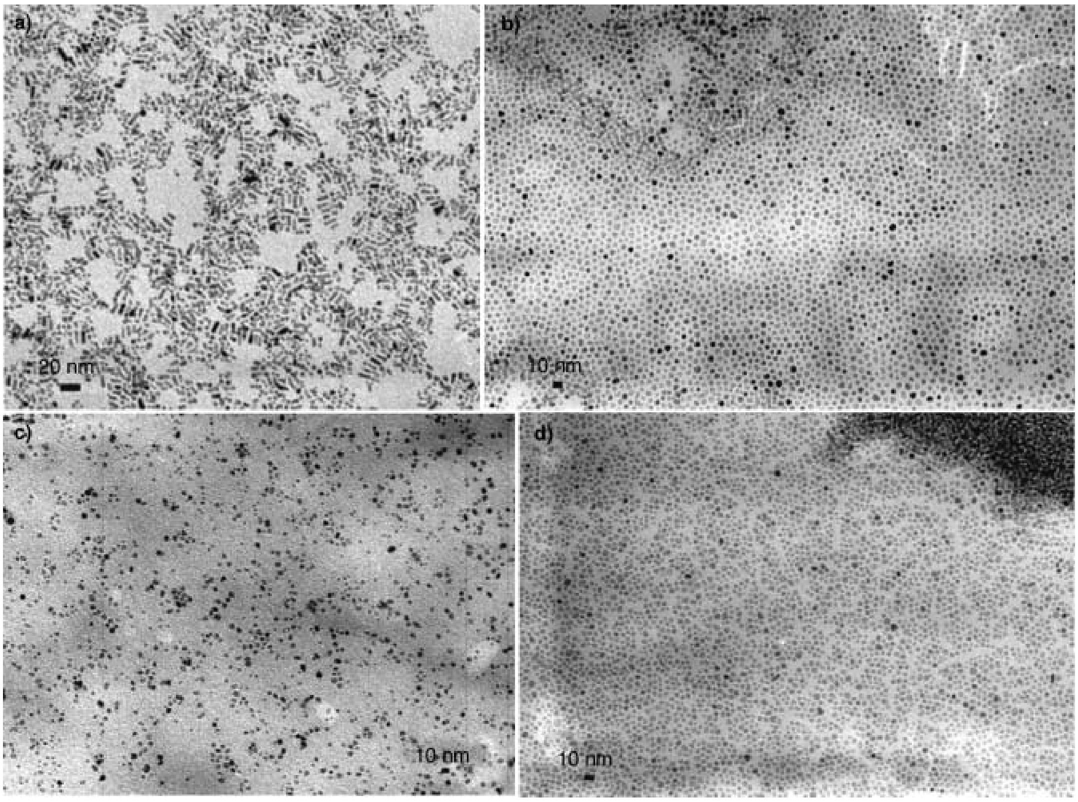

Figure 1. TEM micrographs of ZnO nanoparticles. a) ZnO nanorods grown under standard conditions (see ref. [21]); b) ZnO nanodisks following a slow oxidation/evaporation process in THF (2 weeks); c) ZnO nanodisks using dodecylamine (DDA) instead of hexadecylamine (HDA) as the stabilizing ligand under standard conditions; d) ZnO nanodisks using octylamine (OA) instead of HDA under standard conditions.

Table 1: Summary of the results obtained after oxidation of the [Zn(c-C_6H_{11})$_2$] precursor under various reaction conditions.

Ligand added	Solvent	Time	Overall concentration [M]	Temperature	Size [nm][b]	Morphology
–	THF	Standard[a]	0.042	RT		Agglomerated nanoparticles
HDA	THF	Standard	0.042	RT	$8.1 \pm 3.3 \times 2.6 \pm 0.4$	Nanorods
HDA	THF	Standard	0.125	RT	$11.4 \pm 5.7 \times 2.8 \pm 0.7$	Nanorods
HDA	THF	2 weeks	0.042	RT	4.1 ± 0.9	Nanodisks
HDA	THF	Standard	0.042	45 °C	4.8 ± 0.3	Nanodisks
HDA	THF	Standard	0.01	RT	< 3.0 after 1 day 4.3 ± 0.5 after 4 days	Nanodisks
HDA	THF	5 min under Ar	0.042	RT	$5.8 \pm 1.3 \times 2.7 \pm 0.3$	Nanorods
DDA	THF	Standard	0.042	RT	3.0 ± 0.5	Nanodisks
OA	THF	Standard	0.042	RT	4.0 ± 0.7	Nanodisks
HDA	Toluene	Standard	0.042	RT	4.6 ± 0.9	Nanodisks
HDA	Heptane	Standard	0.042	RT	2.4 ± 0.5	Nanodisks
HDA	–	Standard	–	RT	$10.7 \pm 1.2 \times 1.6 \pm 0.3$	Nanorods
DDA	–	Standard	–	RT	$9.2 \pm 2.0 \times 3.7 \pm 1.8$	Nanorods
OA	–	Standard	–	RT	$7.4 \pm 1.4 \times 2.8 \pm 0.6$	Nanorods
2 HDA	–	Standard	–	RT	~ 5	Not homogeneous
2 DDA	–	Standard	–	RT	$17.1 \pm 3.4 \times 3.0 \pm 0.4$	Nanorods
2 OA	–	Standard	–	RT	$36.9 \pm 10.8 \times 2.8 \pm 0.3$	Nanorods

[a] Standard reaction time is 17 h under Ar and 1 or 2 days of oxidation/evaporation. [b] The values indicate the diameter of nanodisks or the length and width for nanorods; size dispersion is given after the mean size.

oxidation, the amine ligand remains coordinated to zinc and suggests that this coordination participates to the control of the growth of the particles.

The results reported in this communication highlight the possibility of synthesizing crystalline ZnO nanoparticles of controlled morphology at room temperature. If the length, width, or diameter of the particles are well characterized, TEM observations suggest that the particles are in fact plates or disks, which agrees with the layered structure of ZnO. The control of size and shape results from the characteristics of the solutions (presence of amine ligands; presence and nature of the solvent). Quite surprisingly, the zinc oxide nano-objects prepared in this way may change size and shape at room temperature in solution. For example, when carrying out the reaction with HDA, as described in the standard procedure, but with a

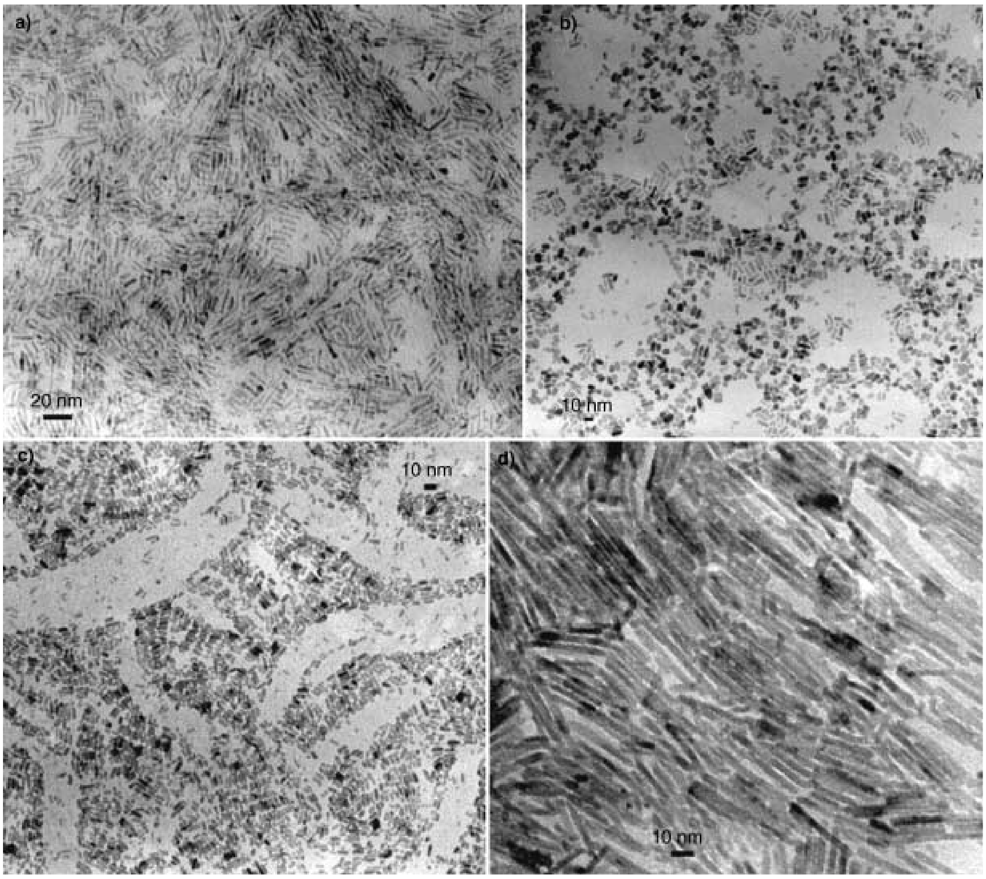

Figure 2. TEM micrographs of various ZnO nanorods, which were prepared using 1 equiv HDA (a), DDA (b), or OA (c) ligands in the absence of solvent; d) long ZnO nanorods obtained in the presence of 2 equiv OA as ligand, in the absence of solvent.

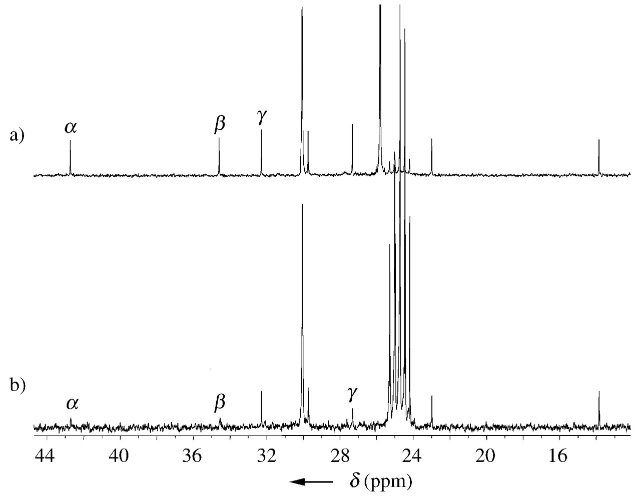

Figure 3. ^{13}C{^{1}H} NMR spectra of a) the free HDA ligand; b) ZnO nanoparticles coated with HDA.

concentration of reagents of 0.01 mol L^{-1}, very small spherical particles are obtained after 24 h (less than 3 nm in diameter), which coalesce into nanodisks of approximately 4.3 nm diameter after 4 days, whereas nanorods form at higher HDA concentrations. This result is in agreement with the findings of Weller et al., where the shape of the ZnO nanoparticles formed were found to be very sensitive to the overall concentration of the precursors, and gave rise to rodlike ZnO particles by "oriented attachment" at high concentrations and quasi-spherical particles at low concentrations.[7] The anisotropic (nanorod) shape is observed either when the particles are synthesized in the presence of one equivalent of HDA in THF under otherwise standard conditions, or with one or two equivalents of amine in the absence of solvent. However, nanorods are not formed when the reaction mixture is heated or if the reaction is allowed to proceed very slowly, which strongly suggests that the rods are kinetic products and, as such, thermodynamically unstable, in contradiction with what has been found for cobalt nanorods.[15] This also suggests that the mesoscopic structure of the solution, present in the conditions described above, but absent when the solution is heated or diluted, may control the growth of the nanorods. The nature of the solvent and of the amine are also important since the growth of rods only occurs with the THF/HDA combination or in the presence of various amines but in the absence of solvent. This again suggests that the organization of the ligand in solution plays a decisive role for the shape control.

All ZnO nanoparticles described in this paper display, at room temperature, both in solution and in the solid state, two emission bands; one near 570 nm and the other near 365 nm, in agreement with previous reports on ZnO particles.[3,22] It is interesting to note that the two emission bands are not quenched by the solvents and that they are intense enough to be directly observed by the human eye (See Supporting Information; S2 and S3).

In conclusion, we have described the unprecedented formation of crystalline zinc oxide nanoparticles in solution at room temperature. The exact mechanism of this astonishing reaction is difficult to assess. In principle, the decomposition in air of the organometallic precursor was expected to lead to an oxidized material. However, the absence of hydroxide formation is surprising and may result from the exothermicity of the oxidation reaction. Furthermore, the crystallinity, the coalescence phenomena, the changes of size and shape observed at room temperature in solution, and the formation of extended monolayers were not anticipated. This suggests that, like metal nanoparticles, oxide nanoparticles display a dynamic behavior in solution. This can be linked to the demonstration of ligand coordination throughout the synthesis process. It is moreover interesting that such semiconducting oxide nano-objects form clear and luminescent organic solutions. Finally, these nanoparticles can easily be deposited on various surfaces as monolayers or thick layers, and may thus be applied as photoluminescent probes or paints.

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[1] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* **2001**, *292*, 1897.

[2] J. Johnson, H. Yan, R. Schaller, L. Haber, R. Saykally, P. Yang, *J. Phys. Chem. B* **2001**, *105*, 11387.

[3] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H. Choi, *Adv. Funct. Mater.* **2002**, *12*, 323.

[4] W. I. Park, G. Yi, M. Kim, S. L. Pennycock, *Adv. Mater.* **2002**, *14*, 1841.

[5] L. Vayssieres, K. Keis, A. Hagfeldt, S. Lindquist, *Chem. Mater.* **2001**, *13*, 4395.

[6] L. Vayssieres, *Adv. Mater.* **2003**, *15*, 464.

[7] C. Pacholski, A. Kornowski, H. Weller, *Angew. Chem.* **2002**, *114*, 1234; *Angew. Chem. Int. Ed.* **2002**, *41*, 1188.

[8] C. L. Carnes, K. J. Klabunde, *Langmuir* **2000**, *16*, 3764.

[9] M. Shim, P. Guyot-Sionnest, *J. Am. Chem. Soc.* **2001**, *123*, 11651.

[10] C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706.

[11] K. Soulantica, A. Maisonnat, M.-C. Fromen, M.-J. Casanove, P. Lecante, B. Chaudret, *Angew. Chem.* **2001**, *113*, 462; *Angew. Chem. Int. Ed.* **2001**, *40*, 448.

[12] K. Soulantica, A. Maisonnat, F. Senocq, M.-C. Fromen, M.-J. Casanove, P. Lecante, B. Chaudret, *Angew. Chem.* **2001**, *113*, 3071; *Angew. Chem. Int. Ed.* **2001**, *40*, 2983.

[13] C. Pan, K. Pelzer, K. Philippot, B. Chaudret, *J. Am. Chem. Soc.* **2001**, *123*, 7584.

[14] N. Cordente, M. Respaud, F. Senocq, M.-J. Casanove, C. Amiens, B. Chaudret, *Nano Lett.* **2001**, *1*, 565.

[15] F. Dumestre, B. Chaudret, C. Amiens, M.-C. Fromen, M.-J. Casanove, P. Renaud, P. Zurcher, *Angew. Chem.* **2002**, *114*, 4462; *Angew. Chem. Int. Ed.* **2002**, *41*, 4286.

[16] C. Nayral, E. Viala, P. Fau, F. Senocq, J.-C. Jumas, A. Maisonnat, B. Chaudret, *Chem. Eur. J.* **2000**, *6*, 4082.

[17] K. Soulantica, L. Erades, M. Sauvan, F. Senocq, A. Maisonnat, B. Chaudret, *Adv. Funct. Mater.* **2003**, *13*, 553.

[18] F. Rataboul, C. Nayral, M.-J. Casanove, A. Maisonnat, B. Chaudret, *J. Organomet. Chem.* **2002**, *643–644*, 311.

[19] M. Monge, M. L. Kahn, A. Maisonnat, B. Chaudret, Fr 03-04285, **2003**.

[20] K. H. Thiele, S. Wilcke, M. Ehrhardt, *J. Organomet. Chem.* **1968**, *14*, 13.

[21] Standard experimental procedure: Both the precursor and the ligand are introduced in equal quantity under argon in a predried solvent (approximately 50 ppm of water is present, as measured by Karl-Fisher volumetric titration ; concentration of each reactant: $0.042\ \mathrm{mol\,L^{-1}}$) and left to react at room temperature for a few hours. The solution is then exposed to ambient air and moisture, generally for one or two days, during which the solvent evaporates and the complex is oxidized and condenses into nanoparticles of zinc oxide (see Figure 1a). The nanoparticles can then be dissolved or suspended again in a solvent for further use. Interestingly, a similar reaction carried out in dry air leads to agglomerated nanoparticles of ZnO displaying no defined size or shape. Increasing the concentration of reagents in solution from 0.042 to $0.125\ \mathrm{mol\,L^{-1}}$ leads to nano-objects of higher aspect ratio. Exchanging THF for toluene or heptane produces nanoparticles of isotropic morphology with mean diameters of 4.6 and 2.4 nm, respectively. A slow oxidation/evaporation process in THF (2 weeks) produces only nanodisks of very homogeneous size (4.1 nm; see Figure 1b). Reducing the reaction time under argon to 5 min, prior to oxidation leads to shorter nanorods $\approx 5.8\times 2.7$ nm in size. Increasing the reaction temperature leads to isotropic disk-shaped nano-objects. Exchanging HDA for dodecylamine (DDA) or octylamine (OA) also leads to disks with mean diameters of 3.0 and 4.0 nm, respectively (Figure 1c and d). Finally, in the absence of solvent, mixing equimolar amounts of **1** and an amine (HDA, DDA, or OA) yields nanorods of 10.7×1.6, 9.2×3.7, and 7.4×2.8 nm, respectively. In this case, doubling the concentration of amine relative to zinc has little effect for HDA but produces nanorods of 17.1×3.0 nm or 36.9×2.8 nm in the case of DDA and OA, respectively (see Figure 2).

[22] A. van Dijken, E. A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink, *J. Lumin.* **2000**, *90*, 123.