Self-Assembly of Cobalt Nanorods

Unprecedented Crystalline Super-Lattices of Monodisperse Cobalt Nanorods**

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Magnetic nanomaterials display new interesting fundamental properties and potentially have many applications.[1–4] One of the most promising applications, high-density information storage, requires spatially separated particles in the nanometer range that act as single magnetic domains, are ferromagnetic at room temperature, and are electrically isolated.[5] In this respect, the preparation of well-ordered two- and three-dimensional (2D and 3D) super-lattices is of crucial importance.[6] Several synthetic routes towards Fe[6] and Co[7,8] nanoparticles have recently been developed, for example, through the decomposition of carbonyl compounds. A high magnetic anisotropy is, however, necessary for spherical nanoparticles to be ferromagnetic at room temperature. This can be achieved, as recently reported, through formation of bimetallic Co/Pt or Fe/Pt nanoparticles.[9–11] Another approach is to use nonspherical nanoparticles which may display large shape anisotropy. Recently, Alivisatos and co-workers described the formation of cobalt nanodisks from the decomposition of $[Co_2(CO)_8]$ in the presence of trioctylphosphane oxide (TOPO) and oleic acid (*cis*-9-octadecenoic acid).[12] At the same time we reported the selective formation of cobalt nanorods and nanowires, as well as the control of their aspect ratio through the decomposition of organometallic precursors in the presence of a mixture of long-chain amines and oleic acid.[13] Anisotropic structures, however, also require organization in 2D or 3D super-lattices to be of practical interest. While the formation of such assemblies from spherical nanoparticles is well-documented,[8,14–18] only a few reports concern the organization of nanorods,[19,20] and the formation of crystalline super-lattices has not been reported.

Our research group has been involved for a long time in the synthesis of nanoparticles from non-carbonyl organometallic precursors.[21–24] Decomposition of such compounds affords by-products that are not detrimental to the intrinsic properties, such as the magnetic moments, of the particles.[22] We have also reported that the use of weakly coordinating ligands may enable the control of shape in solution.[23] This technique has been used for the formation of nickel nanorods in the presence of long-chain amines[24] and, recently, of the cobalt nanorods mentioned above.[13] The exact mechanism controlling both the formation of the rods and their dimensions remain unclear. One striking observation is, however, that the same ligand systems can be used to control the self-assembly of the spherical particles and the shape of the nanorods.

This observation prompted us to try to understand the exact role of the ligand system in shape control and also to finely tune the ligand system to produce monodisperse nanorods that were able to self-assemble. We now report on the formation of unprecedented 2D and 3D super-lattices of monodisperse cobalt nanorods through the decomposition of $[Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})]$[25] in the presence of a mixture of hexadecylamine (HDA) and stearic acid (octadecanoic acid). We also provide evidence for the self-organization of spherical particles prior to coalescence into nanorods.

In a typical reaction $[Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})]$ was decomposed under H_2 (3 bar) in anisole at 150 °C in the presence of a mixture of a long-chain amine and an acid. The reaction with oleic acid and oleylamine has previously been shown to produce spherical nanoparticles after 3 h (3 nm) and nanorods after 48 h (9 × 40 nm). However, agglomerates and well-dispersed particles were present after a reaction time of 3 h. Careful examination of these agglomerates by TEM after preparation of a very thin layer by ultramicrotomy shows the presence of monodisperse nanoparticles with a diameter of 3 nm included in a 3D network (see Supporting Information). Similar super-lattices of tin nanoparticles have been observed previously and were suggested to result from crystallization in solution.[18] The interparticle distance is about 2.5 nm, and areas where coalescence of the particles occurs are evident. This observation, therefore, suggests that coalescence of the particles occurs inside super-lattices, at least in an initial step.

An attempt was made to optimize the monodispersity of the rods by choosing the most suitable ligands and concentrations. The use of lauric acid (dodecanoic acid, C_{12}) and hexadecylamine (1:1:1 Co/acid/amine) leads to the formation of cobalt nanorods with an approximate size of 5 × 85 nm (**1**). Deposition of one drop of a diluted solution of these rods on the microscopy grid resulted in their self-organization into arrays containing approximately 10 parallel nanorods with an interparticle spacing of about 3 nm (Figure 1B). Using octanoic acid (C_8) instead of lauric acid results in the formation of shorter and wider rods (9 × 33 nm; **2**; Figure 1 A). The nanorods produced with stearic acid (C_{18}) have a diameter similar to the previous rods, but are longer (8 ×

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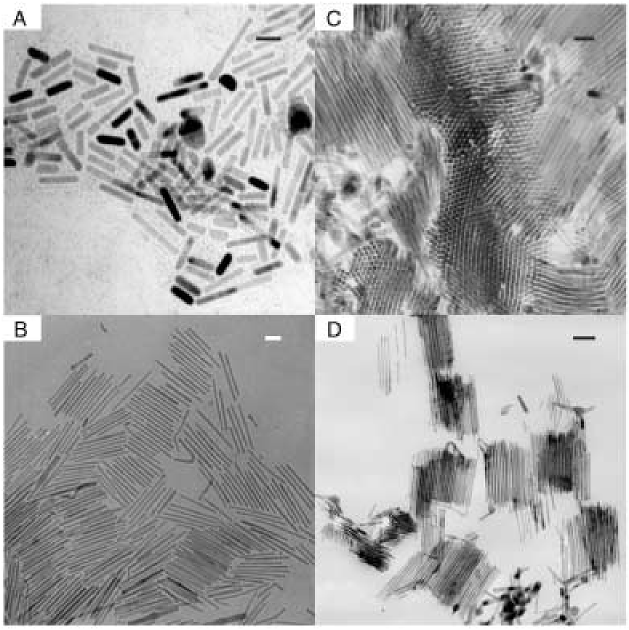

Figure 1. TEM micrographs of nanorods synthesized using hexadecylamine and A) octanoic acid (**2**), B) lauric acid (**1**), and C, D) stearic acid (**3**). The sample used in (C) was prepared by ultramicrotomy. Scale bar: 30 nm.

128 nm; **3**) and more regular in dimensions. Furthermore, the nanorods are organized into unprecedented 3D super-lattices, the largest of which is close to 1 μm (Figures 1 C, D and 2). In each case the nanorods precipitate upon cooling the reaction mixture to room temperature. These super-structures are thus most probably formed from the reaction solution by a crystallization process. Ultramicrotomy shows the almost exclusive presence of such super-lattices in all parts of the sample (Figure 1 C). In addition, their random orientation on the TEM grid allowed the observation, in selected cases, of the hexagonal cross-section of the nanorods (Figure 2 B). The rods are organized in a hexagonal structure with an interparticle distance of approximately 2 nm. This arrangement has been further confirmed by tilting the copper grid in the microscope chamber to bring the growing axis of the nanorod clusters parallel to the electron beam. An interparticle distance of 2.5 nm can also be estimated from the nanorods parallel to the TEM grid (Figure 2 A). The nanorods stabilized by lauric acid and/or stearic acid adopt a parallel orientation between one another. The three sets of nanorods consist of a pure hexagonal close-packed (hcp) cobalt structure, with the *c* axis oriented along the growth direction of the nanorods (Figure 2 C).

From a magnetic point of view, these nanorods display a strong effective anisotropy (K_{eff}) as a consequence of both their shape and crystalline structure, where the *c* axis linked to the hcp phase is parallel to the rod axis.[26] The magnetic moment of the nanorods can be considered as a macro-spin, with a large energy barrier ($\Delta E = K_{\mathrm{eff}}\,v$) between the up and down directions. The volume (v) and high anisotropy of each individual nanorod lead to a blocking temperature well above room temperature.[27] These systems may, therefore, be very interesting for the storage of very high density magnetic data. Accordingly, these materials, like those previously obtained in the presence of oleic acid, display a ferromagnetic behavior at room temperature. Hysteresis loop measurements at 2 K (Figure 3,) show magnetization $\boldsymbol{M}$(5 T) values of 136, 100, and 142 $\mathrm{A\,m^2\,kg^{-}_{Co}}$ for **2, 1**, and **3**, respectively, that are reduced relative to the bulk value ($\boldsymbol{M} = 163\ \mathrm{A\,m^2\,kg^{-1}_{Co}}$) and to the value previously reported for rods not showing any sign of organization, but which display an analogous ligand coating.[25] The hysteresis loops display very different shapes and coercive fields $\boldsymbol{H}_c$ of 740, 3200, and 7200 Oe for **2, 1**, and **3**, respectively. Their remanent magnetization also increases from 0.16 × $\boldsymbol{M}$(5 T) in **2** to 0.5 × $\boldsymbol{M}$(5 T) in **3**. As a general rule, parallel nanorods organized into planar arrays, such as **1**, display an antiferromagnetic coupling of their magnetic moments, while chains of nanorods display a ferromagnetic one.[28,29] The coupling is expected to be stronger within the chains than between the planes. The most favorable organization from a magnetic point of view is that observed in **3**, where ferromagnetic chains of nanorods are coupled antiferromagnetically. The existence of antiferromagnetic couplings could be a possible explanation for the low $\boldsymbol{M}$ values measured for **1–3.** However, a remanent ferromagnetic order can be induced after saturating the sample, and this will be stabilized by the anisotropy of the nanorods. This result explains the high remanent magnetization of **3**. Finally, an open question is whether the magnetic energy could help the self-organisation process and the formation of 3D lattices. Precise calculations will be performed to estimate this.

Long-chain amine and acid molecules (and now, oleic acid and oleylamine) have become standard reagents both for the control of the self-assembly of different metal and semi-

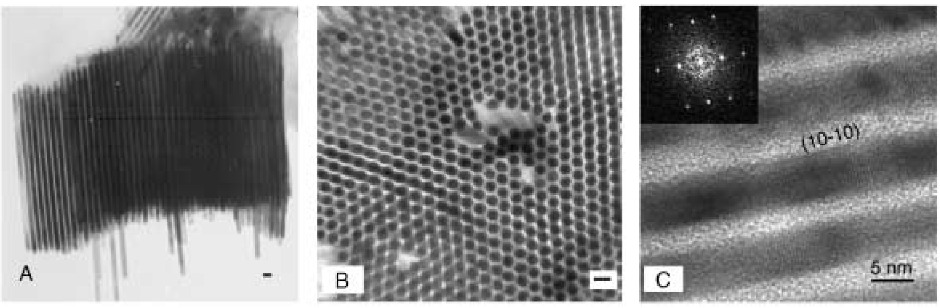

Figure 2. TEM micrographs of self-organized nanorods of **3** (A, B; scale bar: 10 nm). HREM micrograph and electron-diffraction pattern of some aligned rods (C).

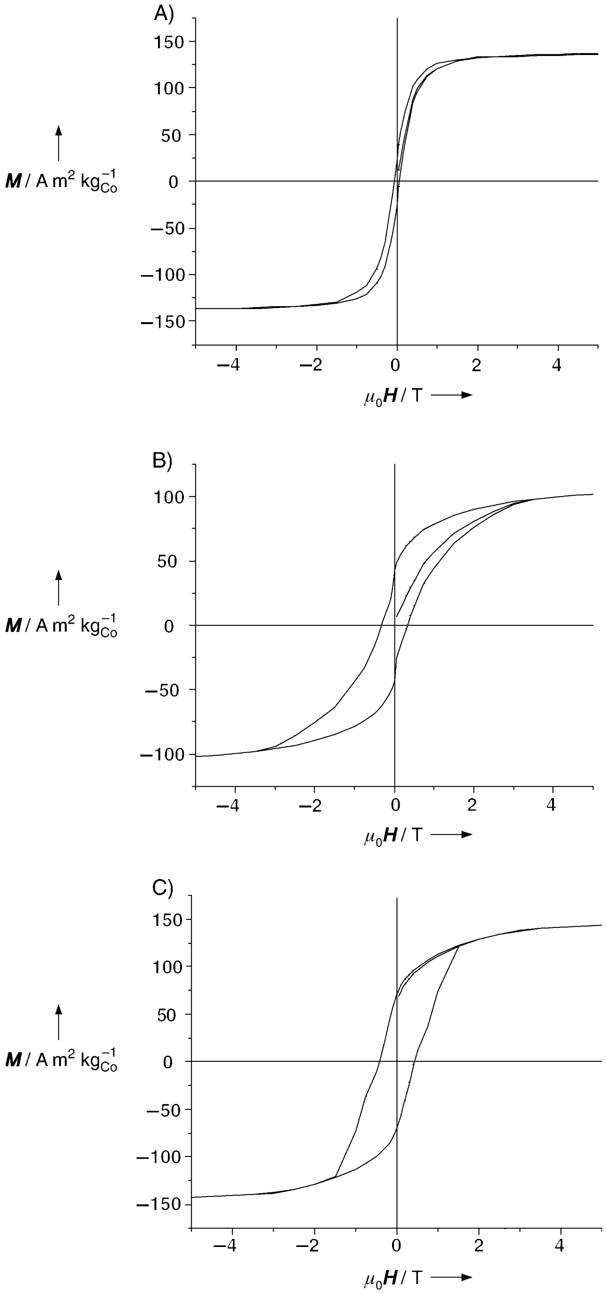

Figure 3. Magnetization curves recorded at 2 K of cobalt nanorods obtained in the presence of: A) HDA and octanoic acid (1:1) (**2**); B) HDA and lauric acid (1:1) (**1**); and C) HDA and stearic acid (1:1) (**3**).

conductor nanoparticles and for the fabrication of nanorods. Monodisperse nanoparticles are produced which assemble into 3D solid super-lattices at the early stage of the reaction. For the oleic acid/oleylamine system we found evidence for the coalescence of some of these particles into rod-shaped particles in a similar way to that observed for particles included inside mesoporous materials.[30] This process could provide seeds for the growth of the rods, although the size of the initial particles (3 nm) is very different from the diameter of the final rods (9 nm). The influence of the chain length of the acid on the dimensions of the rods is not understood. We can, however, point out that gelation has been observed at an early stage of the reaction in the two systems that produce the more regular rods, namely in reactions involving lauric and stearic acid. This gelation could provide a template for the formation of super-lattices of spherical particles and possibly the growth of nanorods. The most important result of this study, the formation of self-assembled nanorods that are strictly monodisperse in terms of both length and diameter, is observed for the longest rods that are obtained with stearic acid (which contains the longest alkyl chain). This system displays bunches of nanorods that are monodisperse in diameter (5 nm) but not in length at the early stage of the reaction, and thus suggests that the coalescence process is facile. In contrast, octanoic acid, which possesses a small alkyl chain, leads to objects displaying smaller aspect ratios. This result may suggest that a good fit of the chain lengths of the acid and amine is necessary to reach monodispersity. The nanorods (**3**) self-organize into 2D and 3D super-structures, inside which they are all aligned in the same direction with a compact, hexagonal arrangement in the perpendicular plane. Some defects are visible, such as the ones shown in Figure 2B. The interparticle distance in these super-structures is approximately 3 nm when using lauric acid and 2–2.5 nm when using stearic acid. The maximum length of a long-chain ligand directly coordinated to cobalt can be estimated to be about 2.5 nm for stearic acid and HDA, and 1.8 nm for lauric acid. This result implies a different organization for rods **2** and **3**. In the case of **2**, the 3-nm interparticle distance and the formation of monolayers of aligned rods suggests a self-organization on the microscopy grid, in a way similar to that observed for several systems of spherical particles.[21] In contrast, the shorter interparticle distance and the observation of 3D super-lattices for **3** implies interdigitation of the alkyl chains of ligands coordinated to different nanorods, which suggests a real process of direct crystallization in solution, as recently found for tin nanoparticles.[18]

In summary, we have demonstrated that the appropriate choice of ligands and alkyl chain lengths enables the synthesis of ferromagnetic nanorods of monodisperse diameter and length from a non-carbonyl organometallic precursor. This in turn allows the formation of unprecedented hexagonal super-lattices of nanorods as a result of crystallization in solution. The formation of these regular nanorods may result from the initial inclusion of monodisperse spherical particles into 3D super-lattices.

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