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Synthesis and Magnetic Properties of Nickel Nanorods

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ABSTRACT

Nickel nanoparticles of tunable shape have been synthesized in THF, in the presence of hexadecylamine (HDA) or trioctylphosphineoxide (TOPO), in mild conditions and characterized by HREM and SQUID measurements. The formation of nanorods is promoted by a high amine content in the reaction medium. In contrast to what is observed for TOPO-protected nickel particles, the saturation magnetization of HDA-capped nanoparticles is comparable to that of bulk nickel, which demonstrates that the coordination of an amine ligand does not alter the magnetic properties of nickel.

Intensive research on magnetic nanomaterials is induced by their expected applications,[1] for example, in high-density magnetic recording or magnetic sensors.[2] A target material is a high-density assembly of magnetic nanorods of high magnetization. This issue would be best achieved for noncontaminated surfaces, as magnetization is highly sensitive to surface contamination. While high yield syntheses of perfectly monodisperse nanoparticles[3] have been achieved, the simultaneous control of their shape and surface state, to control both their anisotropy and magnetization, is still highly challenging.

In our group, we have been interested for a few years in the synthesis of magnetic nanoparticles (Ni[4], Co[5], Co_xPt_{1-x}[6]), taking profit of the tools of organometallic chemistry. Instead of the well-known carbonyl metals, olefinic complexes are used as a source of metal atoms. We have shown that hydrogenation of the olefinic ligands into the corresponding, coordinatively inert alkanes yielded nanoparticles of noncontaminated surface,[4,7] which display magnetic properties analogous to that of clusters prepared in ultrahigh vacuum.[8] In the presence of a stabilizing polymer, only spherical nanoparticles are obtained. However, we have evidenced, in the case of indium, that the shape could be tuned from spherical nanoparticles[9] to nanowires[10] depending on the ligand present in the reacting medium (respectively trioctylphosphineoxide, TOPO, or hexadecylamine, HDA). Few reports deal with the synthesis of nanorods of ferromagnetic metals. Recently, Alivisatos et al.[11] have demonstrated that the use of a mixture of oleic acid and TOPO could produce magnetic nanorods of cobalt at the early stage of the thermal decomposition of $Co_2(CO)_8$. However, the rods are not stable in the reaction medium and transform into spheres with time. Acicular iron particles have also been reported. When their growth proceeds in the presence of tubular lecithin assemblies, the shape selectivity decreases with time.[12] On the contrary, Hyeon et al. have reported the controlled coalescence of spherical iron nanoparticles, protected by TOPO, into nanorods. This process requires a complex mixture of trioctylphosphine and didodecyldimethylammonium bromide in pyridine.[13]

Selective coordination of a ligand on a facet of the first formed nanoparticles has been claimed to be the key for an anisotropic growth of nanoparticles.[11,14] This approach seems very promising; however, the ligands may strongly modify the magnetic properties of the nanoparticles. Hence, it is well known that strong π-acceptor ligands, such as carbon monoxide, induce a dramatic collapse of the saturation magnetization.[1b,5] A recent work by Dreyssé et al.[15] suggests that coordination of amine ligands at the surface of nanoparticles should not reduce their magnetic properties. We have thus investigated the effect of HDA on the shape and magnetic properties of nickel nanoparticles, such as saturation magnetization, and anisotropy, and compare them to results obtained with the widely used TOPO, using the complex $Ni(COD)_2$ (**1**; COD = cycloocta-1,5-diene) as precursor. This precursor has previously been employed for the synthesis of nickel nanoparticles embedded in a polymer[4,16] or

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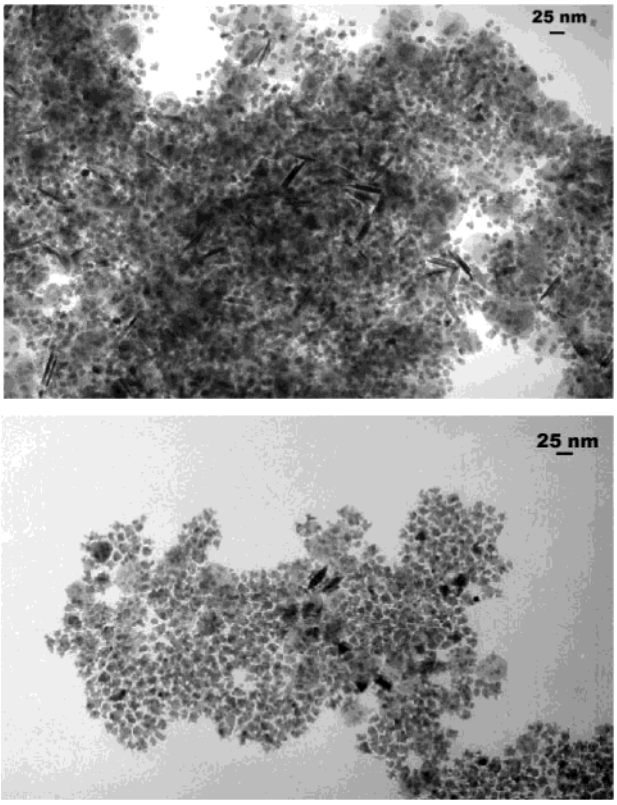

Figure 1. TEM image of nickel nanoparticles synthesized with (top) 0.5 equiv HDA; (bottom) 1 equiv HDA.

amorphous carbon,[17] and recently for the synthesis of carboxylate-protected nickel nanocrystals displaying a trigonal shape.[14]

The reaction of **1** with HDA (1 or 2 equiv per Ni atom) leads to the formation of dark gray colloids. In a typical procedure, 500 mg of **1** (98+%, Strem Chemicals) dissolved in 60 mL THF was reacted at 70 °C for 12 h, under dihydrogen pressure (3bar), in Fischer−Porter bottles in the presence of 1 (or 2) equiv of HDA (99%, Aldrich) per nickel atom. The reaction is very slow at lower temperatures.

The reaction was carried out without any stirring bar to facilitate the recovery of the product after evaporation of the solvent. The product was homogenized by redissolution in pentane before use. When using either 0.5 or 1 equiv HDA, we observed by TEM large, strongly agglomerated nanoparticles of mean size near 12 or 17 nm, without any clear shape, together with a few rods of size of ca. 4 × 50 nm (Figure 1). The magnetic properties of the material prepared using 1 equiv HDA were measured using a SQUID magnetometer. The material is ferromagnetic at room temperature. The coercive field measured at 2 K is small (275 Oe). At this temperature, we have determined a saturation magnetization (Ms) of 60 emu/g_{Ni},[18] i.e., an average value of 0.63 μ_B per nickel atom, close to that found for bulk nickel (0.602 μ_B).

To favor the formation of rod-shaped nanoparticles, we performed the reaction in the presence of 10 equiv HDA. In this case, a new material was obtained, which shows mostly nanorods, homogeneous in size (ca 4 × 15 nm). Figure 2 displays a view of an agglomerate of nanorods. At the

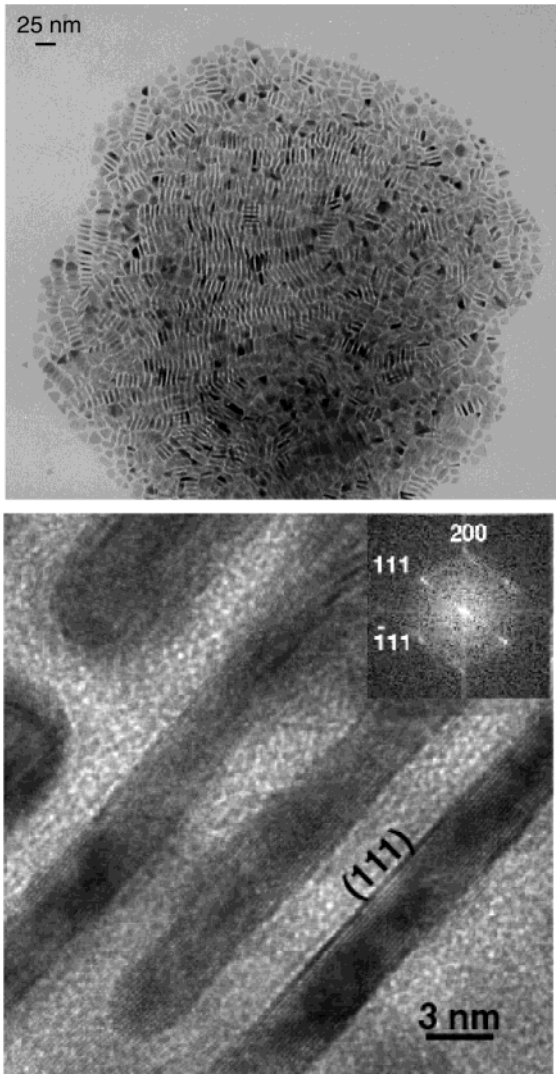

Figure 2. Images of Ni nanoparticles synthesized in the presence of 10 equiv HDA. (top) TEM; (bottom) high-resolution TEM of a nanorods area (included a numerical diffractogram from a single nanorod).

periphery, one can see particles of different shapes, some of which showing a trigonal shape similar to that recently observed.[14]

On the microscopy grid, the nanoparticles are separated by an average distance of 2.5 (± 0.5) nm, in agreement with interpenetrating monolayers of HDA. The nanorods tend to organize with their long axes parallel to one another. The structural orientation of individual nanorods has been investigated by high-resolution TEM. The elongated axis of the nanorods is parallel to a set of (111) planes, which are imaged as parallel fringes spaced by 0.203 nm. The inset, Figure 2, shows the numerical diffractogram (Fourier transform) obtained from the bottom right nanorod. It further evidences its monocrystalline character.

The hysteresis loop of the material measured at 2 K (Figure 3) shows a ferromagnetic behavior with a M_S value close to the bulk value, in agreement with the predicted absence of influence of amine coordination. The decrease of the magnetization at high fields is due to the diamagnetic contribution of the HDA, which has not been subtracted. The

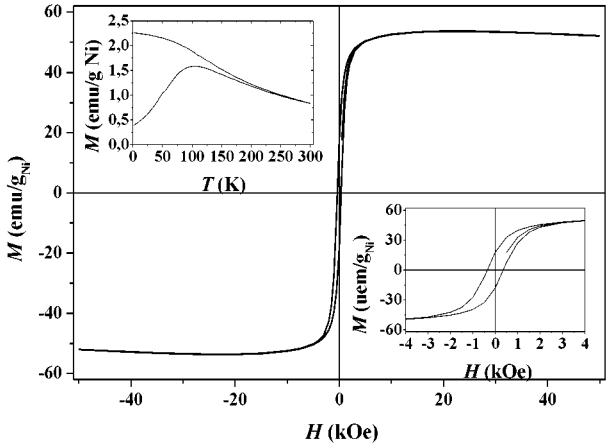

Figure 3. Hysteresis loop for Ni nanorods at 2 K. Insets: (bottom right) enlargement at low field; (top left) ZFC/FC curve (10 Oe).

zero-field-cooling/field-cooling curve (Figure 3) evidences a superparamagnetic behavior above the blocking temperature $T_B = 100$ K. The effective anisotropy of each particle (K_p) can be calculated from T_B, considering the expression given by Dormann et al.:[19]

$$T_B = \frac{(K_p + K_i)V}{(25 + n_1)k_B}$$

where V is the volume of the particle, n_1 is the number of first neighbors around the particle, and K_i represents the contribution of the dipolar interactions to the anisotropy of the system. K_i has been evaluated:[20] $K_i = 9 \times 10^5$ erg/cm^3, considering a compact stacking of the nanorods with six first neighbors at a distance of 2.5 nm, as observed by high-resolution TEM. Thus, the value obtained for K_p, from the expression of T_B, is 14.7×10^5 erg/cm^3. For such rod-shape nanoparticles, the effective anisotropy of each particle is the sum of the contributions of the magnetocrystalline anisotropy (K_u) and of the shape anisotropy (K_s). Thus, knowing the value of the magnetocrystalline anisotropy of bulk nickel taken at 100 K[2c], $K_u = 7.0 (\pm 0.5) \times 10^5$ erg/cm^3, we can calculate a value of 7.7×10^5 erg/cm^3 for K_s.[21] The two values are comparable, therefore it seems that the rodlike shape of the nanoparticles increases the anisotropy by a factor of 2.

Similar reactions attempted with TOPO (1 or 2 equiv per Ni atom) lead to the formation of dark gray colloids. The decomposition of $Ni(COD)_2$ is very fast in this case, so the reaction was carried out at room temperature to ensure reaction times similar to those reported for reactions in the presence of HDA. In a typical procedure, 500 mg of **1** (98+%, Strem Chemicals) dissolved in 60 mL THF was reacted for 12 h at room temperature, under dihydrogen pressure (3bar), in Fischer−Porter bottles in the presence of 1 (or 2) equiv of TOPO (99%, Aldrich) per nickel atom. The reaction was carried out without any stirring bar to facilitate the recovery of the product after evaporation of the solvent.[22] The product was homogenized by redissolution in MeOH before use. As can be seen in Figure 4, TEM

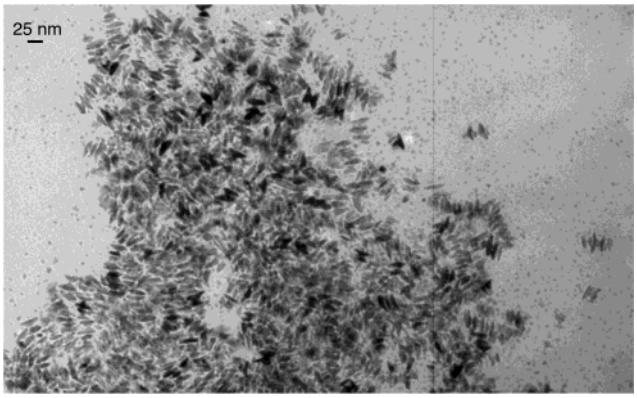

Figure 4. TEM image of nickel nanoparticles obtained in the presence of 2 equiv TOPO.

analysis of the colloids evidences a mixture of small monodisperse spherical nanoparticles and teardrop-shaped nanorods, as described by Alivisatos.[23] Curiously, increasing the TOPO concentration from 1 to 2 equiv results in the formation of smaller spherical particles (respectively 8 and 5 nm) but of larger nanorods (respectively ca. 5×25 and 7×30 nm). Both materials consist of fcc nickel as shown by XRD on bulk samples and electron diffraction on selected areas. No trace of NiO was detected. The magnetic properties of the material prepared using 2 equiv TOPO were measured. The material is ferromagnetic at room temperature. At 2 K, we have measured a coercive field of 500 Oe and a saturation magnetization (Ms) of 35 emu/g_{Ni}, i.e., an average value of 0.37 μ_B per nickel atom. This value is much smaller than the value of 0.602 μ_B found in bulk nickel.[31]P{^{1}H} NMR studies do not evidence the presence of trioctylphosphine in the solution, ruling out any oxygen transfer from phosphorus to nickel and the formation of any antiferromagnetic layer of nickel oxide. In this case, the more probable origin of the low saturation magnetization value is thus attributed to the complexation of the TOPO ligand at the surface of nickel.

In summary, we report in this communication the first synthesis of nickel nanorods outside a template, using only low quantities of HDA as a shape control agent. Increasing the concentration of amine favors the formation of nanorods, nearly monodisperse in diameter, most probably through the specific coordination of the amine.[24] It is noteworthy that in contrast to what has been reported so far,[11,13] the growth of these magnetic nanorods proceeds under very mild conditions of temperature and pressure. Furthermore, we demonstrate for the first time that a pure σ-donor ligand such as an amine does not reduce surface magnetism. In contrast, we find, as previously observed in the case of iron and cobalt, that TOPO induces the formation of both nanoparticles and nanorods. However, the magnetic properties of the material display a low saturation magnetization, which may be related to the coordination of TOPO at the surface of the nickel particles. This is similar to previous observations made upon CO coordination and may also be related to the π-acceptor capability of the TOPO ligand. These results may be of general interest for the production of shape anisotropic particles of various metals and alloys.

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(18) The nickel content in the materials is known from chemical microanalysis. With 0.5 equiv HDA: 41% Ni; 1 equiv HDA: 15.1% Ni; 10 equiv HDA: 2.21% Ni. The saturation magnetization measured by SQUID is then normalized with respect to this nickel content and expressed in emu/g_{Ni}.

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(20) $K_i = n_1 M_S^2 V/d_1^3$ with n_1 first neighbors at a distance d_1.

(21) For nanorods, it is also possible to estimate the shape anisotropy (K_s) according to: $K_s = \delta N M_S^2/2$ where δN is the anisotropic contribution of the demagnetizing factors due to the deviation from sphericity. The value obtained by this way, $K_s = 7.0 \times 10^5$ erg/cm^3, is in good agreement with that determined from the expression of T_B.

(22) Chemical microanalysis gives the nickel content in the final material: 28.8% (1 equiv TOPO); 7.5% (2 equiv TOPO).

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