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Introduction

Nickel nanoparticles (NPs) have attracted a large amount of interest for their magnetic¹ and catalytic² properties due the abundance of Ni compared to other Pt group metals, which inspires research on size and shape control of nanostructures.³ Numerous physical and chemical methods have been used to produce nickel NPs, such as metal evaporation-condensation, electrochemical methods, sonochemical synthesis, metal salt reduction and organometallic precursor decomposition.⁴ The solution processes succeed in producing monodisperse colloidal NPs with controllable sizes by reducing or decomposing metal precursors.

Transition metal NPs from the Pt group show a tunable catalytic activity as a function of nanocrystals size and shape in hydrogenation reactions.⁵ Catalytic activity and selectivity of metal NPs are strongly dependent on their morphology due to the different catalytic activity of exposed planes.⁶ A model system for well controlled shape of metal nanocrystals by solution synthesis has been demonstrated with Pt⁷ and Pd.⁸ These noble metals have a large number of shapes which have been generated and the concept has been extended to Rh.⁹ The principles that direct Pd or Rh nanocrystals growth have yet to be extended to catalytically active 3d metals, especially to Ni. Indeed, 3d transition metals like Ni are slightly more difficult to handle compared to Pd, considering the need for a stronger reducing agent and the occurrence of surface oxidation.

Several strategies have been used to control the shape of nickel NPs, the hard template approach provides an effective route to submicron polycrystalline nanowires and nanor-

Nickel nanocrystals: fast synthesis of cubes, pyramids and tetrapods[†]

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We report the use of organometallic precursors in microwave and microfluidic reactors to synthesize Ni nanoparticles of various shapes: spheres, cubes, trigonal pyramids and tetrapods. Each route has the ability to yield a preferential shape based on kinetic control of crystal growth. Tetrapods are obtained only in a microfluidic reactor. Trigonal pyramids crystallize in the metastable hexagonally close-packed (HCP) phase while spheres, cubes and tetrapods crystallize in the thermodynamically stable face-centred cubic (FCC) phase. The magnetic properties of nanocubes (in particular the magnetic coercive field) are found to be greatly enhanced compared to bulk and previous examples of nanostructured Ni materials.

ods.^{10,11} Another approach combines soft template with inorganic precursors and generally refers to surfactant assisted solvothermal reactions in presence of ligands, ionic surfactants or polymers.¹² Ni(II) salt (mainly Ni(acac)₂) yields spherical NPs in the presence of hydride,^{13,14} long chain amine,^{15,16} polyol^{17,18} or amino-borane reducing agent.¹⁹

Heterogeneous nucleation has yielded Ni NPs with shape control as reported for the synthesis of hexagonal and triangular Ni nanoplates from the catalytic addition of Fe $(CO)_{5}$,^{20,21} seeding of Ni on Mn powders²² and more generally by alloying Ni with other transition metals like Pt.^{23,24}

On the other hand, the use of organometallic precursors has proved to be very efficient in order to synthesize metallic NPs with a clean metallic surface. Organometallic precursors like Ni(cyclooctadiene)₂ (Ni(COD)₂ or Ni(η^4 -C₈H₁₂)₂) have successfully yielded Ni NPs with a broad range of sizes.²⁵⁻²⁸ Hydrogen assisted decomposition of Ni(η^4 -C₈H₁₂)₂ yields a mixture of Ni faceted NPs and nanorods in presence of an excess of hexadecylamine ligand.²⁹ Recently, hydrogen assisted decomposition of metal–organic Ni(acac)₂ has also enabled the formation of Ni nanocubes.³⁰

Reports on size and shape controlled synthesis of nickel NPs are scarce and worthy of investigation, in particular compared to the degree of complexity reached with Pd NPs, Ni nearest neighbor. In order to control the shape of Ni NPs, we chose to investigate the rapid reaction of organometallic Ni precursors to stabilize non-spherical shapes. The use of advanced synthesis tools such as microwave and microfluidic reactors affords reliable and finely tuned synthesis parameters to achieve a high level of control on the kinetics of the reaction. Following this methodology, we report the synthesis of Ni cubes, pyramids, tetrapods. All syntheses are achieved with soft amine ligands which do not quench the surface magnetism and could be removed to yield an active metallic surface.

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Experimental

Materials

Ni(COD)₂ (STREM, 98%) was used as received. 1-Hexadecylamine (HDA) (ACROS, 90%), dodecylamine (Acros, 98%) and triphenylphosphine (STREM, 99%) have been dried, degassed and stored in a glove box. Benzylamine (ACROS, 99%), mesitylene (ACROS, 97%), oleylamine (ACROS, 80–90%), tri-*n*-octylphosphine (Acros, 97%) and octylamine (ACROS, 99%) were dried, degassed and stored on molecular sieve in the glove box.

Synthesis on a heating plate

In a round flask bottle Ni(COD)₂ (0.03 mol L⁻¹) was dissolved in 1-hexadecylamine (10 equiv) and mesitylene, the mixture was heated to 170 °C for 30 min. The same procedure has been carried on changing the temperature, reaction time and ligand. ICP measurements were carried on the powders to measure Ni content.

Microwave oven

 $Ni(COD)_2$ (0.03 mol L⁻¹) was dissolved with 1-hexadecylamine (10 equiv) in mesitylene in a glovebox. The solution was then transferred to a special sealed vial for microwave reaction (CEM Discover) and heated at 170 °C (run time 20 min, hold time from 2 to 60 min). The same procedure has been done while replacing 1-hexadecylamine with different amines chain, oleylamine, octylamine, dodecylamine and benzylamine.

Microfluidic reactor

Ni(COD)₂ (0.03 mol L⁻¹) was dissolved with HDA (10 equiv) in mesitylene. The solution was injected into a microfluidic cell (Syrris glass reactor 250 μ L, three input) using an Asia pump (Syrris) specially designed for flow chemistry with a typical rate of 25 μ L min⁻¹. The reactor was heated to 170 °C on a homemade heating stage equipped with two thermocouples. The same procedure has been done at different injections rates and temperatures.

DSC, TGA, NMR, XRD

10 mg of Ni(COD)₂ powder was placed in a crucible and the measurement was performed under nitrogen from 300 K to 700 K following a heating slope of 10 °C min⁻¹. ¹H NMR spectroscopy: after thermal decomposition of Ni(COD)₂ in 1-octadecene, the solution was filtered and diluted in CDCl₃. ¹H NMR was processed on a 300 MHz Bruker spectrometer. XRD is collected on a Rigaku Ultima IV XRD System. Ni NPs were drop casted on a glass slide.

Electron microscopy

Transmission electron microscopy (TEM) images were obtained from a JEOL-JEM 100SX with 80–100 kV accelerating voltage, high-resolution TEM (HRTEM) images using a JEOL JEM 2100 microscope operating at 200 kV. Samples were prepared by placing a drop of diluted sample on a 400-mesh carbon-coated copper grid.

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SQUID

Magnetic properties were measured using a Superconducting Quantum Interference Design (SQUID) magnetometer MPMS XL7, in the range of temperature 2–300 K and of field 0–5 T. The temperature-dependent susceptibility was measured using DC procedure. The sample was transferred under nitrogen to the SQUID chamber to prevent any oxidation. The sample was cooled to 2 K under zero magnetic field, low magnetic field (5.0 mT) was applied and data collected from 2 K to 300 K (zero-field cooled, ZFC). Field Cooled (FC) measurements were performed from 2 K to 300 K with an applied field during the cooling. Hysteresis loop was measured at 2 K.

Results and discussion

Reaction mechanism

We have studied the decomposition of Ni $(\eta^4-C_8H_{12})_2$ by Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA) and ¹H NMR of the solution after nanoparticles filtration (see Fig. S1-S3†). The DSC data displays an exothermic peak, corresponding to the precursor decomposition, at 80 °C and an endothermic peak, corresponding to the vaporization of cyclooctadiene, at 150 °C. TGA data confirms that the complex is decomposed in Ni metal and two equivalent of cyclooctadiene; the obtained weight loss is very close to the theoretical 78.6% weight loss (21.4% metal content) which is consistent with a complete reaction (Fig. S2[†]). When the thermal decomposition is achieved in 1-octadecene, ¹H NMR spectrum shows that the by-product consists only in cyclooctadiene (Fig. S3[†]). The nickel NPs are therefore synthesized by thermal decomposition of Ni(COD)₂ at a temperature above 80 °C in different ligands in order to control size and shape of the NPs. Moreover, three different types of reactors are used in order to investigate the effect of reaction time on the size, shape and crystallographic structure of the NPs. Apart from the standard flask in a heating mantle, the reaction is also performed in a microwave oven and in a microfluidic reactor.

Size-controlled nickel nanoparticles by ligand screening

Several sets of experiments allow us to understand the roles of the ligands in order to control the size of Ni NPs. For these studies, the concentrations of Ni (η^4 -C₈H₁₂)₂ and amine ligand are held constant, and all the reactions are carried out under N₂ on a Schlenk line or in the glove box to avoid any oxidation. In a typical hotplate reaction or in a microwave oven, nickel NPs are synthesized in the presence of 1-hexadecylamine (HDA) as ligand and mesitylene as solvent. All the reagents are placed in a round bottom flask and heated at a temperature set from 80 °C (decomposition of Ni(η^4 -C₈H₁₂)₂) to 170 °C, boiling point of mesitylene) for different reaction times.

The microwave technique has the potential to greatly contribute to all areas of synthetic chemistry. In particular, the synthesis of NPs and nanostructures, whose growth is highly sensitive to the reaction conditions like temperature and reaction time.^{31,32} Microwave reactions in a nitrogen filled tube allow screening of the influence of different parameters



Fig. 1 Transmission electron microscopy (TEM) images of Ni nanoparticles synthesized in different ligands with a constant ratio precursor/ligand: 1/2 in a microwave at T = 170 °C for 30 min a) octylamine, b) dodecylamine, c) oleylamine and d) hexadecylamine.

on the size and shape of the nanoparticles. The ligands are chosen for their affinity to Ni (amine group) and the rather bulky alkyl or aryl group allow an effective stabilization of the NPs. Trialkylphosphines are also used as bulky ligands to severely limit particle size. Fig. 1 shows the TEM images of Ni NPs obtained with 2 equivalents of ligand per Ni organometallic precursor for a 30 min reaction at 170 °C. In all cases, the colloidal black dispersions are stable for weeks after filtration of the excess of ligand and redispersion in hexane or toluene. The NPs crystallize in the face-centred cubic (FCC) phase with lattice parameters corresponding to bulk Ni (Fm-3m, a =3.52 Å) (JCPDS-04-0850) as shown from X-ray diffractometry (Fig. S4a[†]) and electron diffraction (inset Fig. 1b). Particle size depends primarily on the nature of the functional group. Very small NPs ($D = 2 \pm 1$ nm) are obtained in the presence of triphenylphosphine while the synthesis with trioctylphosphine yields a stable complex (Fig. S4b[†]).

Ni NPs stabilized with primary amines give the following sizes: benzylamine ($D = 4 \pm 2$ nm), octylamine ($D = 3 \pm 2$ nm), dodecylamine ($D = 5 \pm 3$ nm), hexadecylamine ($D = 6 \pm 2$ nm) and oleylamine ($D = 4 \pm 2$ nm) (Fig. 1 and Fig. S4†). Alkylamines yield faceted NPs while increasing the amine chains from octyl to hexadecylamine allows an increase of particle size.

While using hexadecylamine, square and triangular cross section NPs are present along with more spherical NPs (Fig. 1d). The NP shape being clearly linked to the presence of ligand, the amine/precursor ratio has been increased and set to 10/1 in the following experiments.



Fig. 2 TEM and SAED image of Ni nanoparticles in standard flask reaction (sample 2c: HDA/Ni(COD)₂ = 10, T = 170 °C, 2 min).

Shape-controlled nickel nanoparticles with higher hexadecylamine content

Particle shape is kinetically rather than thermodynamically controlled. Therefore, the reaction time and temperature have been monitored from very short (2 min) to long reaction time (240 min) at temperatures ranging from 80 to 170 °C in a standard heating mantle with 10 equivalents of hexadecylamine. Some typical results are shown in Fig. 2 and Fig. S5†, while all the data about synthetic parameters are collected in Table 1.

The results shine a light on the importance of temperature and time of reaction as crucial parameters for controlling size and shape of particles. At low temperatures (below 120 °C), the syntheses yield spherical Ni NPs, a shape already obtained with Ni(η^4 -C₈H₁₂)₂, as reported in the literature.²⁸ The NPs are slightly polydispersed ($D = 5 \pm 3$ nm) and do crystallize in the FCC lattice (Fig. S5a†). Intermediate temperature (T = 150-160°C) yields elongated NPs, nanorods, as the reaction time is extended from 30 to 45 min (Fig. S5b†). The nanorods present an aspect ratio of 5 × 15 nm and crystallize also in the FCC lattice. Previous research²⁹ has shown the formation of nickel nanorods along with the formation of several other shapes.

In the case of our study, temperature and time window have a crucial role in the formation of nanorods. A prolonged heating (240 min) at the same temperature leads to the formation of spherical NPs. Long reaction time involves the reshaping into spherical NPs of nearly the same volume, which is expected from thermodynamic considerations (Fig. S5d†).

At even higher temperature (T = 170 °C), short time reaction yields square, triangular and round shape particles (Fig. 2) as already observed in the microwave experiments at lower ligand content (Fig. 1d).

Table 1 Summary of reaction conditions and results in a standard heating mantle

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Sample	HDA/Ni(COD) ₂	$T/^{\circ}\mathbf{C}$	Reaction time (min)	Morphology	Size (nm)	
2a	10	80-120	30	Spheres	5 ± 3	
2b	10	150-160	45	Rods, spheres	$5*15; 7 \pm 3$	
2c	10	170	2	Triangles, cubes and spheres	5 ± 2	
2d	10	150-170	240	spheres	4 ± 3	

Kinetic control on the yield of shape controlled NPs in microwave and microfluidic reactors

The investigation of Ni NPs synthesis has raised the issue of accurately controlling reaction time in order to improve the yield of a particular shape, which could be achieved in a microwave oven. The reaction under microwave irradiation is conducted at 170 °C with Ni(η^4 -C₈H₁₂)₂ in the presence of 10 equivalents of HDA in mesitylene. Temperature and pressure are monitored during the reaction and Fig. 3 presents TEM images for particles after 2 to 60 min long reaction. Particle size increases slightly with reaction time: $D = 4 \pm 2$ nm (2 min), $D = 5 \pm 2$ nm (20 min), $D = 6 \pm 2$ nm (20 min), $D = 6 \pm 3$ nm (60 min).

TEM images show the effect of reaction time on the amount of triangular cross-sectioned, cubic and spherical NPs formation. While time reaction is gradually increased from 2 to 30 min, the amount of the triangular cross-sectioned particles increases (from 20% to 40%) with a majority of cubic NPs (80 to 60%) (Fig. 3d). Low magnification is reported in the ESI† (Fig. S6). When the reaction is carried out for 60 min, shape controlled particles transform into spherical NPs as already observed on a standard heating plate (Fig. 3c). Post synthesis



In order to investigate the control on the shape of the nanoparticles, the reactions have been carried out in a microfluidic reactor. The flow chemistry in the microfluidic reactor offers a variety of advantages over conventional macroscale chemical processes for the synthesis of metal NPs,^{33–35} including enhanced mass and heat transfer,^{36,37} reproducibility,³⁸ potential for sensor integration for *in situ* reaction monitoring³⁹, rapid screening of parameters, low reagent consumption during optimization, and synthesis parameters independent of the process scale.⁴⁰ The high surface-to-volume ratio of the micro reactor channels enables precise temperature control.

In a typical synthesis, a solution of $Ni(\eta^4-C_8H_{12})_2$ and 10 equivalents of HDA in mesitylene is injected into the glass microfluidic reactor at different injection rates and temperatures. Fig. 4 shows a typical TEM image showing the formation of branched nanoparticles. The synthetic details and summary of results are collected in Table 2.

The reaction time is determined by the injection rate. Since the glass reactor is approximately $250 \ \mu$ L, the reaction time can be compared with the conditions used in the microwave

80% (d) 70% 60% 50% 40% 30% 20% 10% 0% 0 10 20 30 40 50 60 Time (min)

Fig. 3 TEM images of Ni nanoparticles microwave synthesized in 10 equivalents of HDA a) 2 min, b) 30 min c) 60 min reaction, d) plot showing the time dependent shape frequency (\blacksquare for cubic NPs, \blacktriangle for triangular cross-sectioned NPs, \bullet for spherical NPs).



Fig. 4 TEM image of Ni NPs synthesis in microfluidic cell (T = 170 °C for 30 min, sample 4d from Table 2).

Table 2 Reaction conditions in microfluidic reactor

Sample	Injection rate ($\mu L \min^{-1}$)	Reaction time (min)	$T/^{\circ}\mathbf{C}$	Morphology	Size (nm)
4a	100	2.5	170	Triangles, cubes and spheres	7 ± 2
4b	25	10	170	Triangles, cubes and spheres	8 ± 4
4c	25	10	150	Triangles, cubes, spheres, tetrapods	10 ± 4
4d	8	30	170	Triangles, cubes, spheres, tetrapods	$8 \pm 4 \text{ (pod diameter)}$

reaction. For fast reactions (t = 2 min) at 170 °C, the reaction yield cubes and triangular NPs as in MW reaction (Fig. S8a†). Lowering the reaction temperature to 150 °C yields branched NPs along with smaller triangular NPs (Fig. 4). A majority of branched NPs present a three-fold symmetry and the higher contrast in the centre suggests the presence of fourth out-ofplane arm, resulting in a tetrahedral symmetry. These tetrapods coexist with triangular cross-section NPs as already obtained from microwave reaction. Nevertheless, an extended reaction time results in the reshaping of these branched NPs and tetrapods to yield more spherical NPs (Fig. S8d†).

HRTEM and magnetic measurement of the shape controlled NPs

HRTEM has been performed on representative samples of the different shapes observed: spherical, square, triangular and tetrapod shape. Nickel crystallizes in two common compact lattices: most common is the FCC phase and the HCP phase, which has been stabilized in low dimensionality solids like thin films and nanoparticles.

The best yield of nanocubes has been achieved in the microwave (80% cubes, T = 170 °C, 2 min, with 100 equivalents of oleylamine) (Fig. 5a). The cubes self-organize in a square lattice even if the polydispersity prevents long range ordering. Cubic NPs crystallize in the face-centred cubic (FCC) phase with lattice parameters corresponding to bulk Ni (Fm-3m, a = 3.52 Å) (JCPDS-04-0850) (electron diffraction, Fig. 5b). SAED does not show a noticeable decrease of the (111) diffraction ring, expected for aligned nanocubes, which could be explained by the shape polydispersity resulting in the disorder. HRTEM of a single nanocube shows the orientation along the [200] direction. Faces of the cubes consist in the (200) planes.



Fig. 5 Ni cubic NPs from a 2 min MW reaction: TEM (a); SAED (b) and HRTEM of a single NP showing (200) planes (c).

Triangular shape particles have been synthesized with the best yield from microwave reaction (40% triangles, T = 170 °C, 30 min). Fig. 6 shows an HRTEM image of triangular nickel NPs with Fast Fourier Transform (FFT) of a single particle. (100) and (1–10) reflections correspond only to the hexagonally close-packed (HCP) phase with standard lattice parameters (P63/mmc, a = 2.622, c = 4.321) (JCPDS-45-1027). HRTEM shows a large contrast from the centre to the edge, suggesting the NPs are trigonal pyramids rather than flat triangles. Most of the pyramids are truncated on the vertices.

Among all shapes obtained from microfluidic reaction, branched structures are the most frequent shape. The branched structure usually consists in three pods of the same length. TEM image (Fig. 7c) shows a darker region at the centre suggesting the presence of a fourth pod. Tetrapods crystallize in the FCC lattice (Fig. 7b). Each tetrapod is found to be single crystalline and grows along the [111] axis of the FCC lattice (Fig. 7a and inset). A growth process will be proposed in the discussion.

Magnetic measurements have been performed both as dry powders and as frozen dispersion. The latter allow collecting magnetic properties of diluted samples where all magnetic interactions (exchange and dipolar) are not significant. In diluted samples, magnetism arises from a collection of individual NPs and reflects the behaviour of a single average NP. We report below the magnetic properties of samples



Fig. 6 HRTEM of Ni trigonal pyramids; Inset: power spectrum of the area in the square.



Fig. 7 HRTEM of a single tetrapod, inset: respective power spectrum (a), SAED (b) and TEM image of a single tetrapod (c).

synthesized in hexadecylamine with spherical and cubic shape.

Magnetic properties of 4 nm spherical NPs are typical of Ni NPs with a coercive field of 40 mT and a saturation magnetization of 44 A m² kg_{Ni}⁻¹ (bulk values 17 mT, 58 A m² kg⁻¹) (Fig. 8). This high magnetic moment has been obtained thanks to the use of organometallic precursor and soft ligands (amine) which lead to NPs with a magnetic core and shell.



Fig. 8 ZFC/FC ($\mu_0 H = 5.0 \text{ mT}$) (a) and hysteresis (T = 2 K) (b) curves of NPs dispersed in toluene (\blacksquare cubic NPs, \bullet spherical NPs).

The same measurements have been performed on shape controlled NPs. The results displayed are representative of frozen dispersions. 4 nm cubes from microwave reactions display a strong ferromagnetic behavior at low temperature (Fig. 8) with a coercive field of 152 mT, nearly 10 times higher than the bulk values and nearly 4 times higher than the spherical NPs of equivalent size. The magnetic moment is found to be 29 A m² kg_{Ni}⁻¹ at *T* = 2 K, calculated from the volume fraction of Ni NPs obtained from ICP measurements. ZFC maximum (usually called blocking temperature, *T*_B) is found to be *T*_B = 23 K and fitting the ZFC/FC curve using a model of single domain NPs, assuming a magnetic size of 4 ± 2 nm as obtained from TEM, gives a very large anisotropy constant of *K*_{eff} = 7.5 10⁴ J m⁻³.

Discussion on the growth mechanism and magnetic properties of Ni NPs

FCC 4d and 5d transition metals like Pd, Pt, Rh, Ag and Au have been successfully synthesized with different shapes at the nanoscale. In all cases, the structure remains FCC and shape controlled is achieved by controlling the surface energy of the metal using a chemical grafting on the surface of the NPs, density of structural defects and redox potential of the chemical reducing agent. In the present case, the ligand nature (hexadecylamine) and concentration (2 or 10 equivalents relative to the Ni precursor) have been kept constant while temperature is the only relevant parameter towards decomposition of the organometallic precursor. The ligand effectively controls particle size but does not account for the stabilization of different shape (cubes, triangles, tetrapods, rods).

FCC cubic NPs present [200] facets while HCP truncated pyramids mainly have exposed [111] facets. Both shapes transform into spherical NPs upon annealing of colloidal dispersion.

The cubic shape corresponds to previous research on Pd nanocubes structures and to a recent work on Ni nanocubes synthesized by reducing $Ni(acac)_2$ under mild hydrogen pressure.³⁰ As pointed out in the latest study, the growth mechanism of the NP is controlled by the kinetics of the metal-organic precursor.

Tetrapod shape has been obtained only while the reaction is performed in a microfluidic reactor. The pods crystallize in the FCC lattice with growth along the [111] axis. Tetrapods are found to be single-crystalline. Multipods at the nanoscale have been observed for ionic solids like chalcogenides. The growth mechanism of CdSe tetrapods proceeds through the nucleation of a polyhedron (trigonal pyramids, zinc-blende, cubic) which seeds the overgrowth of wurtzite pods on the exposed facets leading to tetrapods.⁴¹ In the case of oxides, the nucleus is a truncated octahedra and the growth of hexapods follows an oriented attachment mechanism.⁴²

Metallic multipods have been synthesized with Rh,⁹ Au⁴³ and Pt⁴⁴ and formation of metallic multipods and controlled platonic shapes has been associated with the competitive growth between [111] and [100] planes in the FCC lattice. The growth rate of each facet can be adjusted through the adsorption of a chemical species on the orthogonal facet (usually a metal ion).

Fig. 9 Schematic diagram of the cubes, truncated trigonal pyramids and tetrapods.

In our synthetic conditions, the formation mechanism of Ni tetrapods is different from the suggested mechanism for other metallic nanostructures since no metallic cation is present in the solution. The formation of tetrapods only occurs in the microfluidic reactor after the formation of pyramidal NPs. One may assume pods growth is promoted by the very fast heating rate, compared to heating plate and microwave oven. The pods grow in the [111] direction, which corresponds to the exposed facets of pyramidal NPs (Fig. 9). The growth mechanism goes through the preferential overgrowth of pods on the vertices of the pyramids. The most plausible growth mechanism consists of the formation of pyramidal NPs follows by preferential overgrowth on the vertices of the structure. Ligands on the vertices are thought to be more labile and allow mass transport from the precursor solution to the vertices, resulting in the growth of pods. The branched NPs then recrystallize in a single crystalline FCC lattice. According to annealing experiments, this morphology is only stable for a short reaction time and rearrange into spheres as reported for Pt multipods.43

In the case of Ni, the change in shape is accompanied with a change in crystallographic phase. Bulk nickel can crystallize into two phases with relatively close energy; the most stable FCC phase and metastable HCP phase. Low dimensionality Ni (thin films and nanoparticles) do crystallize into both lattices and leads to stable HCP phase. NPs have been found to crystallize in the HCP lattice when the reaction is performed at high temperature.^{45,46}

In our study, the structural and magnetic measurements of HCP pyramidal NPs could not be properly measured since the highest yield of pyramids achieved is 40%. XRD and SQUID measurements do not show significant evidence of the presence of HCP phase, which has been observed only by HRTEM on multiple samples. The discrepancy could be due to the nucleation of HCP Ni on a very small scale which prevents macroscopic observation. HCP Ni is observed only for pyramidal NPs and not on any other shape. Therefore, we do believe that the pyramidal NPs obtained result from the nucleation of HCP Ni whereas cubic NPs are obtained from FCC nuclei.

In any case, shape control allows a strong enhancement (ten times) of the coercivity of Ni in the case of cubes (80%) compared with bulk values. 4 nm cubic NPs display a coercive field 4 times larger than the corresponding 4 nm spherical NPs. The enhancement of magnetic anisotropy (from $K_{\text{eff}} = 5.0 \, 10^4 \, \text{J m}^{-3}$ to $K_{\text{eff}} = 7.5 \, 10^4 \, \text{J m}^{-3}$) is consistent with the shape anisotropy of cubic NPs, in addition to the magnetocrystalline

anisotropy of FCC nickel. Our experimental results are consistent with the enhanced anisotropy displayed by Ni nanorods synthesized from hydrogen assisted decomposition of Ni(η^4 -C₈H₁₂)₂ in hexadecylamine.⁴⁷

Compared to a previous report on cubic Ni NPs, the coercivity field is greatly increased from $\mu_0Hc = 10.5$ mT for 12 nm Ni nanocubes³⁰ to $\mu_0Hc = 151$ mT in our measurement on 4 nm Ni nanocubes. The same trend is observed on the magnetic measurements with a magnetic moment of 29 A m² kg_{Ni}⁻¹ compared to the reported value of 12.4 A m² kg_{Ni}⁻¹. Ni nanocubes display large anisotropy and magnetic moment consistent with the use of Ni organometallic precursor which yields large surface magnetism. Therefore, the anisotropy and magnetic magnetic measurement result from core and surface atoms. Anisotropy is found to be the sum of magnetocrystalline, shape and surface magnetism. In our study, two shapes (spherical and cubic) nanoparticles are prepared with the same organometallic precursor and ligands, so that the magnetic properties could be assigned to the NPs shape.

Conclusions

Ni NPs have been synthesized from the thermal decomposition of the organometallic Ni(η^4 -C₈H₁₂)₂. Spherical NPS are formed through addition of alkylamines or triphenylphosphine ligands with a particle size from 3 to 6 nm. Alkylamine ligands can effectively be used for tailoring the shape of NPs quickly using a microwave reactor. The reaction yields cubes up to 80% yield for reactions below 20 min and trigonal pyramids with a yield of 40% for a 30 min reaction. Pyramidal NPs crystallize into the metastable HCP phase as evidenced from HRTEM study. Shape control has also been achieved through microfluidic reaction leading to the formation of single crystalline FCC tetrapods which form in the microreactor through the overgrowth on pyramidal NPs. Tetrapods are stable at room temperature while they rearrange into spheres upon annealing at 150 °C. The magnetic properties of 4 nm nanocubes are greatly enhanced compared to spherical NPs with a very high coercive field of 151 mT and anisotropy constant of 7.5 105 J m-3, respectively 10 times and 50% higher than the bulk values.

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