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The drastic influence of the NaBH₄ reducing agent on the growth of cobalt nanoparticles and their 3D assemblies

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ABSTRACT

Cobalt nanoparticles are synthesized by chemical reduction in reverse micelles using 6 different products of NaBH₄ reducing agent. The nanoparticle size polydispersity strongly depends on the NaBH₄ used. With the same synthetic approach, only one product yields to uniform size and shape nanoparticles. This result highlights that the NaBH₄ plays a key role in the reproducibility of (1) the synthesis of Co nanoparticles characterized by a low size polydispersity, and (2) their 3D assembly. I stress that this finding can strongly affect not only the development of nanoparticles and their 3D assemblies but also our knowledge concerning the nucleation and growth mechanisms at both the atomic and nanoparticle scales, which can be biased, if we do not account this additional key parameter among all the ones involved in the colloidal synthesis.

1. Introduction

3D assembly of inorganic nanoparticles (NPs) into long-range ordered arrays (also called supercrystals) constitutes fascinating advanced nanomaterials [1-4]. Individual NPs act as "artificial atoms" and occupy the lattice sites to form repetitive, periodic "artificial planes". The NP assembly follows the same fundamental principle driving the crystallization of atomic crystals. For example, it has been recently reported that solvent-mediated ligand interactions explain the growth of both nanoparticles as well as supercrystals of NPs [5-8]. Depending on the balance between van der Waals attractions between the NPs and the solvent-mediated interactions between ligands, the supercrystals can grow either heterogeneously on a substrate or homogeneously in solution to give rise either to supercrystalline films or colloidal crystals. The properties of the supercrystals, which can be single- or multi- component, result from the interplay of the intrinsic NP properties and their collective interactions. The intrinsic properties mainly depend on the composition, the size and the shape of the NPs. The collective properties can be controlled by (1) the interparticle distance driven by the ligand, the 3D structure and, if appropriate, the presence of other components and (2) by the 3D structure driven by the ligand, the size and shape of NPs and the growth conditions (temperature, homogeneous or heterogeneous growth) [9]. Thanks to the collective interactions between the NPs, they exhibit new magnetic [10] vibrational [11] mechanical [12] and transport [13] properties and are therefore very promising candidates for the applications. Among other examples, a strong light-matter coupling has been recently evidenced in plasmonic NP fcc supercrystals with applications in nonlinear optics and quantum technology as the quantum information processing, in particular, for ultrafast quantum computation and protected qubits [14]. Lead halide perovskite quantum dot superlattices has been shown to exhibit cooperative radiation processes such as superfluorescence, which could be useful in optoelectronic devices [15]. Also, a very interesting review reports the increased coupling in semiconductor quantum dots solids, inducing high-mobility electronic materials, which leads to record-breaking performance in quantum dot devices, such as electronic transistors and circuitry, optoelectronic light-emitting diodes, photovoltaic devices and photodetectors, and thermoelectric devices [16].

In order to highlight novel properties for novel applications, controlling the organization of the NPs is crucial and constitutes the current fundamental challenge.

The prerequisite of these nanomaterials is the use of NPs with a low size and shape polydispersity. Among the existing approaches to synthesize uniform NPs, the decomposition of organometallic precursors and metal salt reduction, including the micellar approach are the more appropriate to favor uniform NPs, as they meet two fundamental conditions (1) a short nucleation step and (2) a slower step growth of the nuclei. However, many key parameters must be controlled to successfully prepared well-defined populations. In the case of the decomposition of organometallic precursors approach, the NP structural characteristics (the size, the size polydispersity, but also the shape, the crystalline structure and the surface chemistry) depends on the nature of both the precursors, the ligands and the solvent, the heating rate, the reaction time, the reaction temperature, the precursor injection time and the surfactant to precursor ratio [17-19]. In the case of the micellar approach, the size and shape of the NPs are mainly controlled by the nature of both the precursor and the solvent, the water content of the micelles and the relative amount of reducing agent, $R = [\text{NaBH}_4]/[\text{salt precursor}]$ [20,21].

For all these approaches, a potential source of variability in NPs synthesis is the presence of impurities in the purchased reactants. Many researchers involved in this topic have to face this problem. For example, Korgel et al. have reported that the shape of gold NPs synthesized by the seed-mediated, surfactant-assisted, depends on the purchased hexadecylcetyltrimethylammonium bromide (CTAB) purity. They proposed that a very dilute impurity in >99% pure CTABs, disrupts nanorod formation by enhancing the growth rate during the “growth step”, which leads to spherical particles [22]. More recently, Weller at al. have shown that traces of chlorine ions remaining in iron oleate used as the precursor to form iron oxide NPs by the thermal decomposition, or the extractive process used in its synthesis, can dramatically influence the final NP structure (cubes and octapods) [23]. Very recently, Begins-Colin’ group have studied the reproducibility of raspberry-shaped iron oxide nanostructures by a modified polyol solvothermal method. They demonstrated the strong impact of the starting iron chloride precursor (from different commercial origins) as well of the mixing and reaction times on the nanostructure characteristics (diameters,

nanograin size, doping efficiency) [24]. In our group, we have reported the effect of the commercial origin of iron stearate used as precursor in the thermal decomposition approach, on the size and shape of maghemite NPs. An accurate analysis of these impurities allows to explain and propose the growth mechanisms of the spherical, cubic and triangular NPs [25]. Another source of variability in the NP synthesis can result for example from the decomposition of certain products during the process. Hence, Swihart et al. [26] have demonstrated that the use of benzyl ether as solvent in the synthesis of magnetite NPs by the thermal decomposition of iron acetylacetonate ($\text{Fe}(\text{acac})_3$), presents some problems related with its decomposition to benzaldehyde and benzyl benzoate at high temperatures, often leading to unreproducible synthesis. In their paper, after the identification of these “organic impurities”, they show how they can exploit their effects in order to standardizing size- and shape-controlled synthesis of monodisperse magnetite NPs.

Therefore, the presence of impurities in the purchased reactants, can dramatically impact the nucleation and growth mechanisms of the NPs. This leads to the absence of reproducibility of the NP synthesis, which is, however, crucial for their applications [27-29]. While researchers involved in the colloidal synthesis of NPs, have often to face this finding, very few related articles exist.

Here, we focus on the synthesis of Co NPs by the micellar approach. From a fundamental point of view, single-domain magnetic Co NPs, used as building blocks in supercrystals, are of great interest. Such interacting nanoparticles are known to undergo a superparamagnetic (SPM)-superspin glass (SSG) transition at sufficiently high concentrations [30]. Previously, we reported SSG-like magnetic properties of 3D supercrystals characterized by long-range face-centered cubic (fcc) ordering, made of these low anisotropy 8 nm-Co NCs [31]. By further increasing the inter-particle interaction, creating of a long-range ordered state; i.e., superferromagnetic (SFM) state is said to be possible. This magnetic state, never evidenced in real nanomaterials, is expected to have various applications including the magnetocalorimetry.

In this paper, we demonstrate that the use of NaBH_4 as reducing agent, providing either from various or same suppliers, yields markedly changes in the Co NP size, shape and size distribution, synthesized by the micellar approach. This proves that the quality of this

product (degradation / impurities) is a key parameter to produce uniform Co NPs and long-range ordered 3D assembly.

2. Experimental section

The Transmission Electron Microscopy (TEM) study is performed using a JEOL JEM-1011 microscope at 100 kV. The histograms of the NPs are obtained by measuring the diameter of at least 500 NPs deposited on a TEM grid coated with amorphous carbon.

Grazing Incidence Small-Angle X-ray scattering (GISAXS) measurements are carried out using a rotating anode generator operated with a small-size focus (copper anode; focus size $0.2 \text{ mm} \times 0.2 \text{ mm}$; 50 kV, 30 mA). Beam collimation and mono-chromatization is ensured by a parallel beam multilayer graded mirror optic. The sample is mounted on rotation and translation stages and the diffraction patterns are recorded on photo-stimulable imaging plates. Vacuum pipes are inserted between the sample and the imaging plate to reduce air scattering. During GISAXS measurements, the incident beam probes a section ca. 0.8 mm in width and extends along the sample.

3. Results and Discussion

Various approaches provide efficient ways to synthesize uniform Co NPs using Co salts or organometallic complexes as starting materials.

A very efficient and simple soft chemistry route for the preparation of Co NPs is the polyol process taking advantage of the reducing ability of the polyol to reduce Co(II) salts at high temperatures [32]. The presence of a very small amount of a seeding agent such as Ru(III) or Ir(III) chloride [33] has proved to be an efficient method to control the nucleation step and consequently to tune the size and the shape of the resulting particles. Besides the introduction of a nucleating agent, other reaction parameters such as the nature of the polyol, the basicity of the medium, the concentration and the nature of the capping agent or the stirring rate were shown to all have an important influence on the size, shape and structure of the NPs [34,35]. The thermal decomposition of carbonyl metal complexes, via hot injection approach, generates uniform Co NPs [36,37]. For example, Alivisatos et al. demonstrated that the thermolysis of the complex Co_2CO_8 , in the presence of ligands

(combination of the amine, oleic acid and phosphine), induces the formation of different size and shape NPs. Hence, by adjusting the conditions of the reaction and time, it is possible to adjust the relative populations of the ϵ -Co spheres and the hcp-Co disks. However, a mixture of crystalline phases was observed. The authors explain that “to obtain a pure fraction of hcp-Co disks containing no ϵ -spheres, it is necessary to physically separate the two populations after the reaction is quenched” [36]. High temperature, solution phase reduction of cobalt chloride in the presence of a reducing agent (superhydride) and a pair of stabilizing agents (oleic acid and trialkylphosphine), allows also the formation of spherical monodisperse ϵ -Co NPs [38,39]. Murray et al. have demonstrated that shorter the chain of the alkylphosphine they use, larger the NPs which size ranges from 2 to 11 nm [38]. Chaudret and co-workers have reported the synthesis of hcp-cobalt NPs by reacting organometallic cobalt complexes, such as $[\text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\eta^4\text{-C}_8\text{H}_{12})]$ and $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in anisole [40,41]. For example, by using the thermal decomposition of the organometallic complex $[\text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\eta^4\text{-C}_8\text{H}_{12})]$, in the presence of a pair of ligands (long chain alkylamine and long-chain carboxylic acid), they highlighted a shape control of Co NPs. Spheres, rods and multipods are obtained depending on the conditions employed. Nevertheless, this method employs air-sensitive precursors and 3 bars of H_2 , which demands working under inert conditions and using pressure vessels, respectively [40,41].

Very recently, Petit et al. reported a synthetic pathway requiring no reducing sources or heating to produce homogeneous spherical hcp-Co NPs by using the $\text{ClCo}(\text{PPh}_3)_3$ precursor. Involving a disproportionation process, this fast (6 min) synthesis is performed in the presence of tridecanol as ligand. Depending on the halide substituent on the complex, the NPs size can be varied from 2.7 to 8.7 nm [42]. Due to the use of a phosphine as capping agent, Co NPs are however air-sensitive [43].

These various approaches need specific synthetic conditions which can be a high temperature, reductive atmosphere or additional reagents (nucleation seeds, etc.). Some of them also require a long reaction time of up to 2 days. In addition, some solvents and reagents involved in these syntheses can cause pollution and safety issues (toxic or

explosive gases, etc.). The air-sensitivity of some precursors requires specific storage and working conditions. Besides, these approaches use either a combination of two or three ligands involving phosphine, amines or oleic acid, or a single ligand which is not necessarily the oleic acid. However, phosphine and amines used as capping agents, provide a less efficient stabilization against oxidation of cobalt NPs, compared to the fatty acids. In addition, keeping in mind the possible use of the Co NPs as building blocks in supercrystals, the ideal candidate to play the role of capping agent is a fatty acid, used alone (for instance, oleic acid or dodecanoic acid). However, for the approaches mentioned above, the ligands are introduced in the reactant medium from the beginning of the synthesis (either in the ligand form or through the precursor itself), which means that they cannot be changed, otherwise the growth mechanism is expected to drastically change also.

The micellar approach allows the formation of uniform cobalt nanospheres with tunable size at room temperature [44,5] in a microemulsion composed of water in oil droplets [45,46]. Previous studies we made, highlighted the parameters playing a key role on the size and size polydispersity of the Co NPs [44,5]. Tunable size NP (from 3.9 to 9.3 nm) can be obtained by controlling the nature of the solvent. The evolution of the nanoparticle size with the solvent is explained by solvent-mediated ligand–ligand interactions using Hansen solubility parameters. The size polydispersity is controlled by the ratio $R = [\text{NaBH}_4] / [\text{Co}(\text{AOT})_2]$. The $\text{Co}(\text{AOT})_2$ (cobalt(II) bis(2-ethylhexyl)sulfosuccinate) salt used is synthesized in the laboratory [47] and is stable over years either in its solid or liquid form. The reduction of this Co salt is carried out with sodium borohydride. The ligand, used as capping agent, is the dodecanoic acid, which, thanks to its covalent interaction with the Co metal, ensures a very high stability against oxidation and coalescence of the Co NPs, which remain non-oxidized for at least one year. We noted that, from a purchased dodecanoic acid product to another, the quality of the NPs remains unchanged. Once the established synthesis conditions described below are respected, the sources of variability of the quality of the populations of Co NPs are few and related to the reducing agent, NaBH_4 : (1) in order to be efficient, it has to be used immediately after its preparation, which consist to a solubilization

in water for 10 min and (2) the NaBH₄ has to be pure. The importance of the NaBH₄ purity is demonstrated in this paper.

3.1. Effect of the NaBH₄ reducing agent on Co nanoparticles growth. Dodecanoic acid coated Co NPs are synthesized by using the micellar approach.²⁰ The detailed description of the experimental process, divided into five steps, is given hereinafter:

(1) Reverse micelles preparation: 3 ml of a micellar solution is prepared in a centrifuge tube (15 ml) by solubilizing cobalt (II) bis(2-ethylhexyl)-sulfosuccinate, Co(AOT)₂ [47] in isooctane, at a concentration equal to 5 · 10⁻² M. 170 μl of water is added to reach a water content, $w = [\text{H}_2\text{O}]/[\text{Co}(\text{AOT})_2] = 32$. Sample is vigorously shaken and after few minutes, isotropic solution made of reverse micelles is obtained [45].

(2) Reduction step: 5 ml of an aqueous solution of sodium borohydride (NaBH₄) used as reducing agent is prepared in a bottle of 10 ml, at a concentration of 1 M. Its solubilization is performed under stirring for 20 min. Immediately after, 900 μl of this solution is added into the micellar solution, that in turn gives a relative amount of reducing agent, $R = [\text{NaBH}_4]/[\text{Co}(\text{AOT})_2]$, equal to 6. The sample is vigorously shaken for few seconds inducing a change in the solution color from pink to black, indicating the formation of colloidal cobalt nanoparticles.

(3) Nanoparticle passivation : 20 min after the NaBH₄ adding, passivation of the Co NPs with dodecanoic acid molecules is performed. 5 ml of the surfactant solution is prepared in isooctane, in a bottle of 10 ml, at a concentration of 1 M, under stirring, around 1h before using. 1ml of this solution is added to the colloidal solution. Sample is vigorously shaken and let during 20 min in order to ensure the total exchange between the initial surfactant, AOT, and dodecanoic acid at the surrounding of the NPs, aiming to prevent any coalescence between NPs.

(4) Washing step: The solution is washed with ethanol three times with a centrifugation step each time.

(5) Co nanoparticles extraction : After washing, the NPs are dispersed in hexane. The solution is then centrifuged in order to precipitate the largest Co particles whereas the smallest Co nanoparticles are collected.

Some drops of the colloidal solution are deposited on a transmission electron microscopy (TEM) copper grid coated with amorphous carbon.²³

All these steps are carried out in a nitrogen glove box at a temperature equal to 20°C.

Six dodecanoic acid coated Co NP syntheses are performed with the same recipe described above. The only change from one synthesis to the next is NaBH₄ that can come from either various producers or various products from a given producer. The six syntheses (with the six NaBH₄) are performed simultaneously. To check the reproducibility of the results, the series of six syntheses is repeated 3 times.

Figures 1A, 1B and 1C show the TEM images of Co NPs synthesized with NaBH₄ from *three different suppliers*: ACROS, FISHER SCIENTIFIC and ALDRICH respectively. As shown on this figure, both the size distribution of spherical NPs and the presence (or not) of a second population composed of deformed particles drastically depend on the NaBH₄ supplier. From ACROS, spherical NPs characterized by a low size distribution, i.e., 8.7% are obtained (Inset Fig. 1A) whereas from FISHER (Figure 1B and inset Figure 1B) and ALDRICH (Figure 1C and inset Figure 1C) the size distributions are equal to 13.3% and 22.9% respectively. As observed in the TEM images and the size histograms (Table 1, aserix), the increase in the size distribution, σ , is clearly induced by an increase in the smallest size population that leads to a decrease in the mean diameter of the spherical nanocrystals from 7.7 to 6.9 and 6.6 nm. In addition to the nanospheres, we observe the formation of deformed NPs, which proportion increases from 3 to 22 and 24%. This result tends to indicate that the purity of the NaBH₄, which is the main difference between the three reducing agent producers, drastically impacts the quality of the NPs.

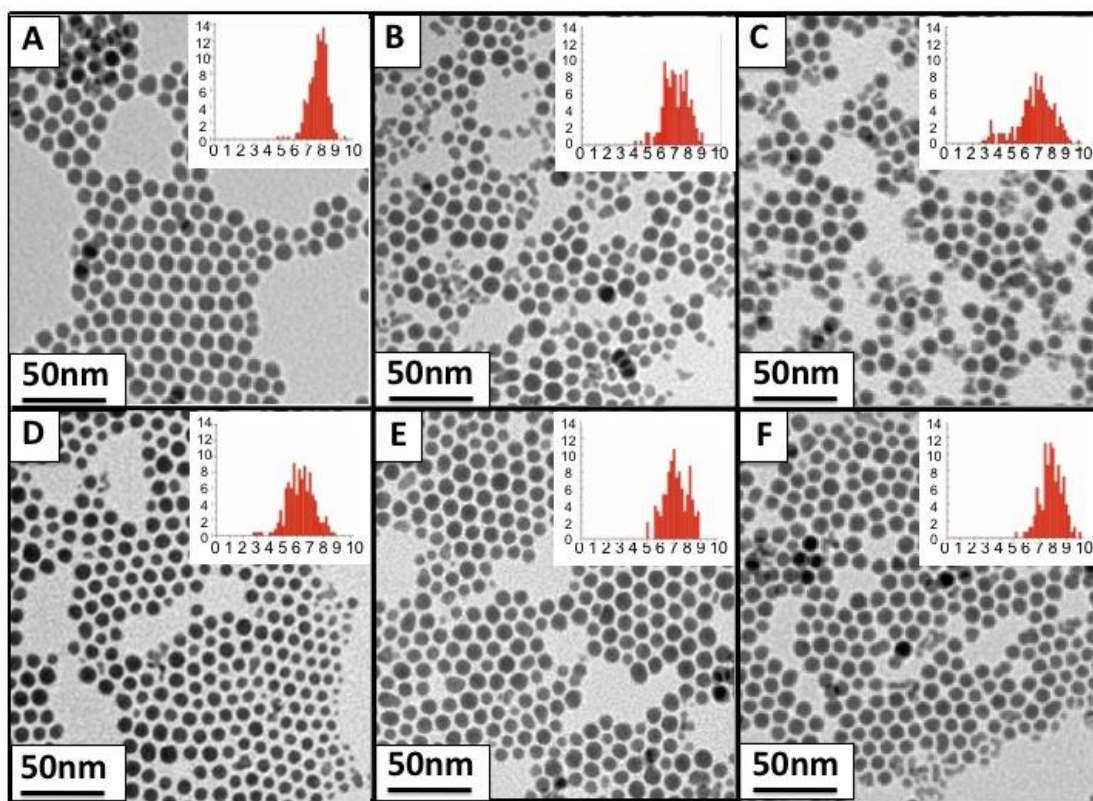


Figure 1. TEM images of cobalt nanoparticles synthesized using NaBH_4 from different producers, products and lots: (A) ACROS 200050250, lot A0256016 (B) FISHER SCIENTIFIC S/2560/46, (C), ALDRICH 21,342-2, (D) ACROS 189301000, lot: AO259700, (E) ACROS 200050250, lot: AO257735, (F) ACROS 200051000, lot: AO257735. Insets: corresponding size histograms of cobalt nanoparticles.

In order to go further in our approach, we carried out other syntheses by using *exclusively* NaBH_4 from ACROS, tested as the producer favoring the lower NP size distribution (Fig. 1A). The populations obtained by using two different products significantly differ. The product referenced as 189301000 (purity: 98%) yields to a spherical population (Figure 1D) with a size distribution of 16.6% (Inset Figure 1D) whereas with 200050250 product (purity: 99%) also spheres are produced (Figure 1A) but with a size distribution of 8.7% (Inset Figure 1A). The increase in the size distribution is due to an increase in the small NP population (around 2 and 3 nm in diameter) inducing a decrease in the mean diameter from 7.7 nm to 6.2 nm. Besides, the percentage of deformed nanocrystals increases from 3% to

8% (Table 1). This result further confirms the importance of the NaBH₄ purity on the NP growth.

	SUPPLIER S	PRODUCT S	LOTS	CATALOG PURITY	MEAN DIAMETER OF SPHERICAL NPS (D ± 0,2) nm	SIZE DISTRIBUTION OF SPHERICAL NPs	PERCENTAGE OF DEFORMED NPS (± 1%)
A	ACROS	200050250	A0256016	99 %	7.7* 7.3 7.5	8.7 %* 9.5 % 11.0 %	3 %* 2 % 3 %
B	FISHER SCIENTIFIC	S/2560/46	0749089	>98 %	6.9* 6.7 7.2	13.3 %* 15.5 % 13 %	22 %* 25 % 20 %
C	ALDRICH	21,342-2	S44825-428	99 %	6.6* 5.8 6.0	22.9 %* 24.1 % 19.5 %	24 %* 27 % 22 %
D	ACROS	189301000	A0259700	+98 %	6.2* 5.7 5.5	16.6 %* 17.2 % 18.0 %	8 %* 10 % 7 %
E	ACROS	200050250	A0257735	99 %	7.0* 6.7 7.2	12.7 %* 12.0 % 14 %	10 %* 9 % 13 %
F	ACROS	200051000	A0257735	99 %	7.8* 7.0 7.5	10.4 %* 9.5 % 13 %	10 %* 13 % 9 %

Table 1. Structural parameters of Co nanoparticles synthesized by the micellar approach, with six different NaBH₄ from different producers, products and lots. (* values extracted from the series of TEM images presented in Figure 1. Other values are extracted from two other series of syntheses).

Finally, let us focusing on the synthesis made with *various lots from the same ACROS product* referenced as 200050250. From the same identified product, producer and purity. Figures 1A, 1E and Table 1 illustrate various populations of NPs. The use of NaBH₄ from the lot AO256016 and AO257735 yields to Co NPs with a mean diameter and size distribution equal to 7.7 nm / 8.7 % and 7.0 nm / 12.7 % respectively. This result suggests that either the purity of NaBH₄ from a given producer varies from lot to lot, or the storage conditions from their fabrication to their sale are not always optimal yielding to degradation of the molecule. For example, it is well known that presence of trace of water strongly

affects NaBH₄ and consequently its efficiency as reducing agent. That could explain the two different populations obtained by using two different NaBH₄ referenced nevertheless as *the same lot AO257735*. The size distributions of spherical NPs and percentages of deformed one's found are 12.7% and 10% and 10.4 % and 10% respectively (Figures 1E, 1F and Table 1). The change of the product reference of the two NaBH₄ i.e. 200050250 and 200051000 indicates, as a first ascertainment, a change in the product conditioning, in the first case, the weight is 25g against 100g in the second one. Nevertheless, we observe that these two reducing agents are less optimal compared to the one allowing population characterized by a size distribution equal to 8.7 % (Figure1A).

The series of six syntheses have been repeated three times. Considering the same order of the mean diameter and size distribution of the spherical NPs, and the percentage of deformed ones, reported on Table 1 for each series, one can conclude to the high reproducibility of these results.

This result highlights the drastic importance of the origin of the purchased NaBH₄ on the reproducibility of uniform Co nanospheres.

3.2. Chemical instability of NaBH₄. The possible origin of the non-reproducibility of uniform Co nanosphere syntheses. Because the series of the syntheses (with the six NaBH₄) are performed simultaneously with the same protocol described below in the paper (for instance, with the same protocol to solubilize in water the various NaBH₄), the dependency between the structural parameters (the size, the shape and the size and shape polydispersity) of the Co NPs with the NaBH₄ used, is clearly established. The absence of reproducibility of this synthesis, with NaBH₄ can be explained in terms of degradation of this product.

From the literature, it is well established that NaBH₄ is highly stable in the solid state, but it is very hygroscopic [48]. At ambient temperatures, it starts to adsorb water at a low relative humidity, 20% [49], to finally transform into the dihydrate NaBH₄.2H₂O, which remains stable up to 40°C [50]. However, during a prolonged contact with the air moisture, NaBH₄ begins to dissolve in the adsorbed water, which induces its hydrolysis and then the subsequent accumulation of sodium borates impurities [48,51]. Decomposition of NaBH₄ in the air in the presence of moisture was observed to be accelerated by increasing temperature

and under the action of carbon dioxide [52]. Therefore, the degradation of certain NaBH₄ products could be explained by the non-optimal storage conditions in terms of temperature and moisture atmosphere, before their shipping in the laboratory.

The purification of the reducing agent NaBH₄ have been discussed in the literature. For example, in a recent paper, Netkina et al. [53], propose an improved purification by using a new approach to re-crystallize NaBH₄ from a solution in diglyme with gaseous ammonia at the stage of NaBH₄ dissolution in order to increase its solubility. Nevertheless, such process remains very complicated and the final purity is around 90% at best, which is less than the purity of the purchased products we use (See Table 1). In their paper, they conclude that their results demonstrate the importance of further efforts towards the creation of new methods for NaBH₄ purification and the improvement of the existing ones. Therefore, at present, we cannot consider purifying the purchased NaBH₄ products before using them. However, it is important to detect the “wrong” products. We emphasize that the “good” one’s are highly stable over several years without specific storage conditions. They are just kept in their closed bottle, at room temperature.

The presence of impurities in NaBH₄ can have a negative influence in two different ways: (1) the NaBH₄ could be less efficient as reducing agent, (2) the impurities could impact the nucleation and growth of the NPs through specific adsorption in cobalt crystalline facets.

Regardless of the synthesis approach and the nanomaterials, our finding contributes to the broader field of nanoparticle chemical synthesis, warning about the possible influence of impurities in the products (purchased or home-made). Presence of impurities can either induce formation of poor-quality of NPs (a large size and shape polydispersity) or, at the opposite, induce specific structural characterizations (size and shape for example). Therefore, this parameter is crucial to correctly interpret the obtained results, i.e., to highlight the key parameters of a given chemical approach and then valid it. It is also important to detect a possible problem of impurities in the products in order to propose highly-reproducible synthesis, which is the prerequisite for their applications. To date, the reproducibility of the synthesis of NPs remains an important challenge, which can be partly explain by the presence of undesirable impurities in the chemical products.

3.3. Effect of the NaBH₄ reducing agent on supercrystals of Co nanoparticle growth.

We have developed deposition procedure which allows the elaboration of long-range fcc ordered 3D assemblies of Co NPs [3], also called supercrystals. After their synthesis, the concentration of the dodecanoic acid coated NPs dispersed in hexane was fixed at 5.5×10^{-7} M. Highly Ordered Pyrolytic Graphite (HOPG) substrates (10 mm x 5 mm) are horizontally immersed in 200 μ l in this colloidal solution. The solvent evaporation takes place at 25 °C under a nitrogen flow, and lasts around 6 hours. When the deposition is made with Co NPs (ACROS 200050250, lot A0256016), the grazing incidence small-angle X-ray scattering (GISAXS) pattern shows reflections characteristic of a highly crystallized fcc structure growing in the [111] direction (Figure 2A) [3]. From the (111) reflection, we deduce a periodicity of the lying planes equal to 8.7 nm, giving a center-to-center interparticle distance equal to 10.7 nm, and then an interparticle gap of 3.0 nm. However, the same deposition made with Co NPs from (ALDRICH 21.342-2, lot S44825-428), shows a totally different behavior as the GISAXS pattern (Figure 2B) shows a diffuse ring typical of the absence of any long-range crystalline order. This result is explained by the too large size and shape polydispersity of Co NPs, which hinder their 3D self-organization.

This result reinforces the drastic impact of the NaBH₄ product on the growth processes, not only at the atomic scale but also at the nanoparticle scale.

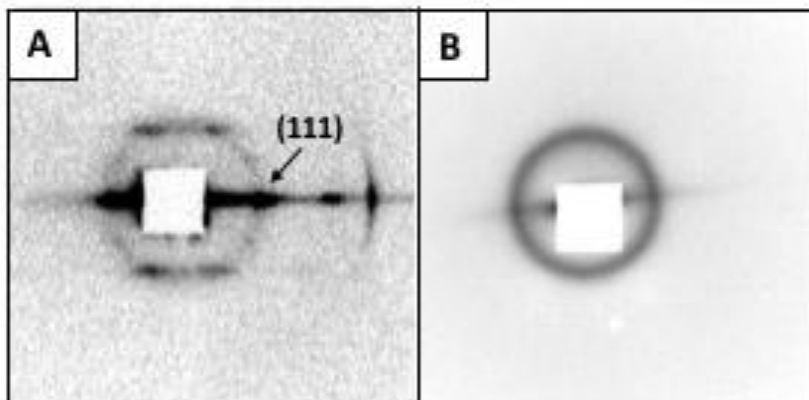


Figure 2. Diffraction patterns of 3D assemblies made with cobalt nanoparticles from (A) ACROS 200050250, lot A0256016 and (B) ALDRICH 21.342-2, lot S44825-428.

4. Conclusions

In this paper, for the first time, we report that one key parameter in the reproducibility of uniform spherical Co NPs synthesized by the micellar approach, is the origin of the purchased reducing agent, NaBH₄. Depending on the supplier, on the product and even on the lot of the product of NaBH₄, we observe either uniform spherical Co NPs or size and shape polydisperse NPs. This dramatic result, never reported in the literature is explained in terms of the degradation in certain NaBH₄, leading to the non-uniform NP populations, and then, hindering long-range NP organization in supercrystals.

Regardless of the synthesis approach and the nanomaterials, our finding warns against the possible influence of impurities in the products (purchased or home-made) which can strongly impact the formation of NPs, either in a positive or negative way. Therefore, this parameter is key to correctly interpret the obtained results, i.e., to highlight the key parameters of a given synthesize approach and then to propose highly-reproducible synthesis, which is the prerequisite for their applications.

In the micellar approach, the ligands used as capping agent, are added at the end of the NP synthesis, therefore, this approach offers the possibility to tune these ligands. In light of this, potential future direction for research in this field is to study the impact of the ligands differing by their nature and length chain on their interactions with their environment (solvent, polymer, nanoparticle). Controlling for instance the ligand length chain of the Co NPs organized in supercrystals is of great importance to tune the structural characteristics of these nanomaterials, i.e., the interparticle distance and the 3D cristalline structure. Therefore, these magnetic superlattices provide a new horizon in fundamental physics and are used as model systems for considering phenomena related to dipolar interactions within the solid and in particular the dipolar superferromagnetism (SFM), expected in a highly dense supercrystals.

REFERENCES

- [1] Bishop, K. J. M.; Wilmer, C. E.; Soh, S.; Grzybowski, B.A. Nanoscale Forces and Their Uses in Self-Assembly. *Small* 2009, 5, (14), 1600–1630.
- [2] Boles, M. A.; Engel, M.; Talapin, D. V. Self-Assembly of Colloidal Nanocrystals: From Intricate Structures to Functional Materials. *Chem. Rev.* 2016, 116, (18), 11220–11289.
- [3] Lisiecki, I.; Albouy, P.A.; Pileni, M. P. Face-centered cubic supracrystalso of cobalt nanocrystals. *Adv. Mater.* 2003, 15, 712-716.
- [4] Costanzo, S.; Ngo, A. T.; Russier, V.; Albouy, P. A.; Simon, G.; Colombari, Ph.; Salzemann, C.; Richardi J.; Lisiecki, I. Enhanced structural and magnetic properties of fcc colloidal crystals of cobalt nanoparticles. *Nanoscale* 2020, 12, 24020–24029.
- [5] S. Costanzo, G. Simon, J. Richardi, Ph. Colombari, and I. Lisiecki, Solvent effects on cobalt nanocrystal synthesis. A Facile Strategy to control the size of Co nanocrystals, *J. Phys. Chem. C* 120 (2016) 22054–22061.
- [6] Goubet, N.; Richardi, J.; Albouy, P. A.; Pileni, M. P. How to predict the growth mechanism of supracrystals from gold nano- crystals. *J. Phys. Chem. Lett.* 2 (2011), 417–422.
- [7] A.-T. Ngo, S. Costanzo, P.A. Albouy, V. Russier, S. Nakamae, J. Richardi, I. Lisiecki, Formation of colloidal crystals of dodecanoic acid coated γ -Fe₂O₃ nanocrystals experimental and theoretical investigations, *Colloids Surf. A* 560 (2019) 270–277.
- lisiecki
- [9] S. Lee, A.-T. Ngo, I. Lisiecki, A. Courty, Structural diversity in binary superlattices from Au and γ -Fe₂O₃ nanocrystals: towards fine tuning of dipolar interactions, *Mater. Chem. Front.* 6 (2022) 1814-1823.
- [10] Parker, D.; Lisiecki, I.; Salzemann C.; Pileni, M. P. Emergence of new collective properties of cobalt nanocrystals ordered in fcc supra-crystals: II- Magnetic Investigation. *J. Phys. Chem. C*, 2007, 111, 12632–12638.
- [11] Courty, A.; Lisiecki, I.; Pileni, M.P. Vibration of self-organized silver nanocrystals. *J. Chem. Phys.* 2002, 116, 8074–8078.

- [12] Gauvin, M.; Yang, N.; Barthel, E.; Arfaoui, I.; Yang, J.; Albouy, P.A.; Pileni, M.P. Morphology, nanocrystallinity, and elastic properties of single domain ϵ Co supracrystals. *J. Phys. Chem. C* 2015, 119, 7483–7490.
- [13] Urban, J.; Talapin, D.V.; Shevchenko, E.V.; Kagan, C.R.; Murray, C.B. Synergism in binary nanocrystal superlattices leads to enhanced P-type conductivity in self-assembled PbTe/Ag₂Te thin films. *Nat. Mater.* 2007, 6, 115–121.
- [14] N.S. Mueller, Y. Okamura, B.G.M. Vieira, S. Juergensen, H. Lange, E.B. Barros, F. Schulz, S. Reich, Deep strong light–matter coupling in plasmonic nanoparticle crystals, *Nature* 583 (2020) 780-784.
- [15] G. Rainò, M.A. Becker, M.I. Bodnarchuk, R.F. Mahrt, M.V. Kovalenko, T. Stöferle, Superfluorescence from lead halide perovskite, quantum dot superlattices, *Nature* 563 (2018) 671-675.
- [16] C.R. Kagan, C.B. Murray, Charge transport in strongly coupled quantum dot solids, *Nature Nanotechnology* 10 (2015) 1013-1026.
- [17] Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. Synthesis of Monodisperse Spherical Nanocrystals. *Angew. Chem.* 2007, 46, 4630 – 4660.
- [18] Wu, L.; Mendoza-Garcia, A.; Li, Q.; Sun, S. Organic Phase Syntheses of Magnetic Nanoparticles and Their Applications. *Chem. Rev.* 2016, 116, 10473–10512.
- [19] Estrader, M.; Soulantika, A.; Chaudret, B. Organometallic Synthesis of Magnetic Metal Nanoparticles. *Angew. Chem. Int. Ed.* 2022, 61, e202207301.
- [20] Lisiecki, I. Size, Shape, and Structural Control of Metallic Nanocrystals. *J. Phys. Chem. B* 2005, 109, 12231-12244 12231.
- [21] Eastoe, J.; Hollamby, M. J.; Hudson, L. Recent advances in nanoparticle synthesis with reversed micelles. *Advances in Colloid and Interface Science* 2006, 128–130, 5–15.
- [22] Smith, D. K.; Korgel, B. A. The Importance of the CTAB Surfactant on the Colloidal Seed-Mediated Synthesis of Gold Nanorods. *Langmuir* 2008, 24, 644-649.
- [23] A. Feld, A. Weimer, A. Kornowski, N. Winckelmans, J.P. Merkl, H. Kloust, R. Zierold, C. Schmidtke, T. Schotten, M. Riedner, S. Bals, H. Weller, Chemistry of shape-controlled iron oxide nanocrystal formation, *ACS Nano* 13 (2018) 152-162.

- [24] P.D. Ramirez, C. Lee, R. Fedderwitz, A.R. Clavijo, D.P.P. Barbosa, M. Julliot, J. Vaz-Ramos, D. Begin, S. Le Calvé, A. Zaloszc, P. Choquet, M. A. G. Soler, D. Mertz, P. Kofinas, Y. Piao, S. Begin-Colin, Phosphate capture enhancement using designed iron oxide-based nanostructures, *Nanomaterials* 13 (2023) 587.
- [25] S. Meftah, A.T. Ngo, A. Shahmanesh, A. Courty, D. Kondo, F. Bedoui, I. Lisiecki, Stricking effect of the iron stearate purity on the shape and size of maghemite nanoparticles, Submitted to *Colloids Surf. A*.
- [26] L. Qiao, Z. Fu, J. Li, J. Ghosen, M. Zeng, J. Stebbins, P. N. Prasad, M. T. Swihart, Standardizing size- and shape-controlled synthesis of monodisperse magnetite (FeO) nanocrystals by identifying and exploiting effects of organic impurities, *ACS Nano* 11 (2017) 6370–6381.
- [27] N. Mohammad Mahmoodi, S. Keshavarzi, M. Ghezelbash, Synthesis of nanoparticle and modelling of its photocatalytic dye degradation ability from colored wastewater, *Journal of Environmental Chemical Engineering* 5 (2017) 3684-3689.
- [28] Z. Hosseinabadi-Farahania, H. Hosseini-Monfareda, N. Mohammad Mahmoodi, Graphene oxide nanosheet: preparation and dye removal from binary system colored wastewater, *Desalination and Water Treatment* 56 (2015) 2382-2394.
- [29] N. Mohammad Mahmoodi, Z. Hosseinabadi-Farahani, H. Chamani, Dye Adsorption from Single and Binary Systems Using NiO-MnO₂ Nanocomposite and Artificial Neural Network Modeling, *Environmental Progress & Sustainable Energy* 36 (2017) 111-119.
- [30] P. Nordblad, Non-equilibrium dynamics in fine magnetic particle systems, *J. Phys. D: App. Phys.* 41 (2008) 134011.
- [31] D. Parker, I. Lisiecki, M.P. Pileni, Do 8 nm Co nanocrystals in long-range-ordered face-centered cubic (fcc) supracrystals show superspin glass behavior? *J. Phys. Chem. Lett.* 1 (2010) 1139.
- [32] F. Fiévet, S. Ammar-Merah, R. Brayner, F. Chau, M. Giraud, F. Mammeri, J. Peron, J.-Y. Piquemal, L. Sicard, G. Viau, The polyol process: a unique method for easy access to metal nanoparticles with tailored sizes, shapes and compositions, *Chem. Soc. Rev.* 47 (2018) 5187–5233.

- [33] R.K. Ramamoorthy, A. Viola, B. Grindi, J. Peron, C. Gatel, M. Hytch, R. Arenal, L. Sicard, M. Giraud, J.-Y. Piquemal, G. Viau, One-Pot Seed-Mediated Growth of Co Nanoparticles by the Polyol Process: Unraveling the Heterogeneous Nucleation, *Nano Lett.* 19 (2019) 9160–9169.
- [34] K.A. Atmane, C. Michel, J.-Y. Piquemal, P. Sautet, P. Beaunier, M. Giraud, M. Sicard, S. Nowak, R. Losno, G. Viau, Control of the anisotropic shape of cobalt nanorods in the liquid phase: From experiment to theory... and back, *Nanoscale* 6 (2014) 2682–2692.
- [35] K. Mrad, F. Schoenstein, H.T.T. Nong, E. Anagnostopoulou, A. Viola, L. Mouton, S. Mercone, C. Ricolleau, N. Jouini, M. Abderraba, L.M. Lacroix, G. Viau, J.-Y. Piquemal, Control of the crystal habit and magnetic properties of Co nanoparticles through the stirring rate, *CrystEngComm.* 19 (2017) 3476–3484.
- [36] V. F. Puentes, D. Zanchet, C. K. Erdonmez, A. P. Alivisatos, Synthesis of hcp-Co nanodisks” *J. Am. Chem. Soc.* 124 (2002) 12874-12880.
- [37] Y. Bao, W. An, C. H. Turner, K. M. Krishnan, The critical role of surfactants in the growth of cobalt nanoparticles, *Langmuir* 26 (2010) 478–483.
- [38] S. Sun, C. B. Murray, Synthesis of monodisperse cobalt nanocrystals and their assembly into magnetic superlattices, *J. Appl. Phys.* 85, (1999) 4325-4330.
- [39] Y. Su, X. OuYang, J. Tang, Spectra study and size control of cobalt nanoparticles passivated with oleic acid and triphenylphosphine, *Appl. Surf. Sc.* 256 (2010) 2353-2356.
- [40] F. Dumestre, B. Chaudret, C. Amiens, M.C. Fromen, M.J. Casanove, P. Renaud, P. Zurcher, Shape control of thermodynamically stable cobalt nanorods through organometallic chemistry, *Angew. Chem. Int. Ed.* 41 (2002) 4286-4289.
- [41] N. Liakakos, B. Cormary, X. Li, P. Lecante, M. Respaud, L. Maron, A. Falqui, A. Genovese, L. Vendier, S. Koïnis, B. Chaudret, K. Soulantica, The big impact of a small detail: Cobalt nanocrystal polymorphism as a result of precursor addition rate during stock solution preparation, *J. Am. Chem. Soc.* 134 (2012) 17922–1793.
- [42] A. Sodreau, A. Vivien, A. Moisset, C. Salzemann, C. Petit, M. Petit, Simpler and cleaner synthesis of variously capped cobalt nanocrystals applied in the semihydrogenation of Alkynes, *Inorg. Chem.* 59 (2020) 13972–13978.

- [43] M. Alberto Ávila Gutiérrez, A. Moisset, A.T. Ngo, S. Costanzo, G. Simon, P. Colombari, M. Petit, C. Petit, I. Lisiecki, Influence of the nanocrystallinity on exchange bias in Co/CoO core/shell nanoparticles, Submitted to J. Coll. Surf. Sc..
- [44] Lisiecki, I.; Pileni M. P. Synthesis of Well-Defined and Low Size Distribution Cobalt Nanocrystals: The Limited Influence of Reverse Micelles. *Langmuir* 2003, 19, 9486-9489.
- [45] I. Lisiecki, P. André, A. Filankembo, C. Petit, J. Tanori, T. Gulik-Krzywicki, B. W. Ninham, M. P. Pileni, Mesostructured fluids. 1. Cu(AOT)₂-H₂O-Isooctane in oil rich regions, *J. Phys. Chem. B* 103 (1999) 9168-9175.
- [46] I. Lisiecki, P. André, A. Filankembo, C. Petit, J. Tanori, T. Gulik-Krzywicki, B. W. Ninham, M. P. Pileni, Mesostructured fluids. 2. Microstructure and supra-aggregation, *J. Phys. Chem. B* 103 (1999) 9176-9189.
- [47] Petit, C.; Lixon; P.; Pileni, M.P. Structural study of divalent metal bis(2-ethylhexyl) sulfosuccinate aggregates. *Langmuir* 1991, 7, 2026, 1598-1603.
- [48] A.M. Beaird, T.A. Davis, M.A. Matthews, Deliquescence in the hydrolysis of sodium borohydride by water vapor, *Ind Eng Chem Res* 49 (2010) 9596e9.
- [49] M. Murtomaa, E. Laine, J. Salonen, O. Kuusinen, On effects of ambient humidity on sodium borohydride powder, *Powder Handling Process* 11 (1999) 87e90.
- [50] Y. Filinchuk, H. Hagemann, Structure and properties of NaBH₄·2H₂O and NaBH₄, *Eur J Inorg Chem* (2008) 3127e33.
- [51] N. Stepanov, V. Uvarov, I. Popov, Y. Sasson, Study of by-product of NaBH₄ hydrolysis and its behavior at a room temperature, *Int J Hydrogen Energy* 33 (2008) 7378e84.
- [52] J.-H. Kim, K.-T. Kim, Y.-M. Kang, H.-S. Kim M.-S. Song, Y.-J. Lee, et al. "Study on degradation of filamentary Ni catalyst on hydrolysis of sodium borohydride" *J Alloys Compd* 379 (2004) 222e7.
- [53] A.M. Ozerova, O.V. Komova, S.A. Mukha, V.I. Simagina, G.V. Odegova, S.S. Arzumanov, O.A. Bulavchenko, O.V. Netskina, An improved purification of NaBH₄ from storage- induced impurities by ammonia assisted crystallization in diglyme, *International journal of hydrogen energy* 45 (2020) 30756e30766.