



Controlling the crystal structure of Ni nanoparticles by the use of alkylamines

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ABSTRACT

Ni nanoparticles were prepared via thermal decomposition of nickel acetate tetrahydrate in the presence of long-chain amines, which acted as both solvents and reducing agents. By tuning the reaction temperature, Ni nanostructures with either hcp or fcc crystal structure were obtained. In principle, higher temperatures favored the formation of hcp nanoparticles. The employment of additional surfactants such as 1-adamantanecarboxylic acid and trioctylphosphine-oxide facilitated the tuning of the particles' growth limit. The size of the particles varied between 5 and 120 nm. The magnetic features of fcc-Ni nanoparticles were quite similar to the corresponding 'bulk' ones. On the other hand, the hcp-Ni particles showed weak magnetic features, reflected by low magnetization values, the absence of saturation magnetization and by blocking temperatures far below room temperature.

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1. Introduction

Bulk nickel (Ni) is a ferromagnetic transition metal that naturally crystallizes in fcc structure with a lattice parameter of 0.352 nm. Ni films are widely used in electronics, chemical cells, battery and aerospace industry applications due to their ability to withstand corrosion and high temperatures [1]. Concerning nanostructured nickel, it has recently attracted much attention owing to its potential applications in magnetic sensors, memory devices, conducting materials and catalysis [2]. As a result of their considerable scientific and practical interest, various 'wet-chemistry' approaches have been applied for the preparation of Ni nanoparticles with fcc or hcp crystal structures. However, while fcc-Ni nanoparticles have been quite well studied, there are fewer reports for hcp-Ni nanostructures, also taking into account that free hcp-Ni has never been found in nature and it can only be produced by synthetic routes. The magnetic properties of fcc-Ni nanostructures with various morphologies, such as spherical nanoparticles and nanorods have been investigated by Chaudret and co-workers who reported that the amine-capped structures had magnetization values comparable to the corresponding 'bulk' ones [3,4]. On the other hand, it seems really challenging to study the magnetic behavior of hcp-Ni nanoparticles, as up to now there are several different results on the magnetism of hcp-Ni nanoparticles prepared by solution-phase chemical ways: non-magnetic [1], antiferromagnetic [5] and ferromagnetic [6] features

have been reported. Moreover, there are contradicting theoretical reports on the magnetic properties of Ni with hexagonal crystal structure [7]. The role of amines as both solvents and reductants has been examined during the thermal decomposition of Ni precursors aiming to produce Ni nanoparticles with a desired crystal structure. More specifically, in the presence of amines such as dodecylamine, oleylamine and trioctylamine, it has been described that by manipulating synthesis conditions such as the reaction temperature, type of solvent and heating rate, it was able to control the crystal phase of the nanoparticles.

Herein, we use a facile one-pot chemical synthetic protocol for the controlled synthesis of fcc and hcp-Ni nanoparticles, aiming to better understand the role of amines as a factor governing the crystal structure and morphology of the obtained nanomaterials. The synthesis procedure is based on the thermal decomposition of nickel acetate tetrahydrate [Ni(ac)₂·4H₂O] in primary and tertiary amines. In some cases additional surfactants such as 1-adamantanecarboxylic acid (ACA) and trioctylphosphine-oxide (TOPO) were employed to explore their influence on the size and shape of the particles. By tuning the reaction temperature, we were able to fabricate Ni nanoparticles with tailored crystal structures depending mainly on the intensity of heating and surface structure reconstruction due to size reduction. We present and discuss the magnetic behavior of the produced hcp and fcc-Ni nanoparticles compared to the bulk Ni.

2. Experimental

The thermolytic reduction of Ni(ac)₂·4H₂O in long-chain amines yielded Ni nanostructures with various sizes and structure-

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al formations. ACA and TOPO were added in some cases so as to investigate their impact on particles' growth. The maximum reaction temperatures varied in the region 215–330 °C. Table 1 summarizes the experimental details for each one of the prepared samples. In a typical procedure (e.g. sample S2 of Table 1), 550 mg $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$ (2.2 mmol), 360 mg ACA (2 mmol) and 154 mg TOPO (0.4 mmol) were inserted in a three-neck flask in the presence of oleylamine (30 ml). The mixture was degassed with Ar flow for 20 min under stirring. Following this, it was heated to 135 °C and maintained at this temperature for 30 min. In the beginning, the color of the solution was dark green due to the initial color of the nickel precursor. Secondly, the mixture was further heated up to 290 °C at a rate of 4 °C min⁻¹. During the progress of the heating and at ~195 °C the color of the solution turned to black, implying the formation of the Ni nuclei. After 1 h-aging at 290 °C, the mixture was allowed to cool at room temperature. The solid product was precipitated by centrifugation with acetone and washed repeated times with a mixture of hexane and excess acetone. Finally the particles were stored into hexane. To obtain transmission electron microscopy (TEM) images, drops of the colloidal dispersions were placed on carbon-coated copper grids. A 100 kV JEM 100CX microscope was used to study the morphological properties of the particles. Information regarding the structural properties of the synthesized nanoparticles was

received by X-ray powder diffraction (XRD) with a Philips PW 1820 diffractometer using CuK_α radiation. Hysteresis loops and zero field cooled–field cooled (ZFC–FC) curves were acquired by a Superconducting Quantum Interference Device (Quantum Design MPMS-5 SQUID) and a Vibrating Sample Magnetometer (1.2H/CF/HT Oxford Instruments VSM) at the temperature range 10–300 K. Quantitative determination of the organic mass content of the samples was implemented by thermogravimetric analysis (TGA) in a SETARAM SetSys-1200 instrument from room temperature to 1000 °C at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the XRD patterns for the samples S1–S5. Samples S1 and S2, that were isolated from the higher temperature procedures, contain Ni particles that are crystallized in the hcp structure, while milder thermal treatment, samples S3 and S4, resulted in the formation of fcc-structured particles. The absence of Ni-oxide peaks indicates the protective capping role of the amines against oxidation in agreement with relevant studies [2,6]. Thus, we may conclude that the formation of pure hcp-structured

Table 1
Chemical reagents and reaction temperatures for the preparation of Ni nanoparticles^a.

Sample	Ni precursor	Surfactants	Solvent	Temperature (°C)
S1	$\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$ (2 mmol)		OA (30 ml)	330
S2	$\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$ (2.2 mmol)	ACA, TOPO (2, 0.4 mmol)	OA (30 ml)	290
S3	$\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$ (2 mmol)		OA (30 ml)	215
S4	$\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$ (1.1 mmol)	ACA, TOPO (1, 0.2 mmol)	DBE, HDA (15 ml, 13 g)	255
S5	$\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$ (2 mmol)	ACA, TOPO (2, 0.4 mmol)	TOA (30 ml)	290

^a OA = Oleylamine, ACA = 1-adamantanecarboxylic acid, TOPO = trioctylphosphine-oxide, DBE = Dibenzyl ether, HDA = Hexadecylamine, TOA = Trioctylamine.

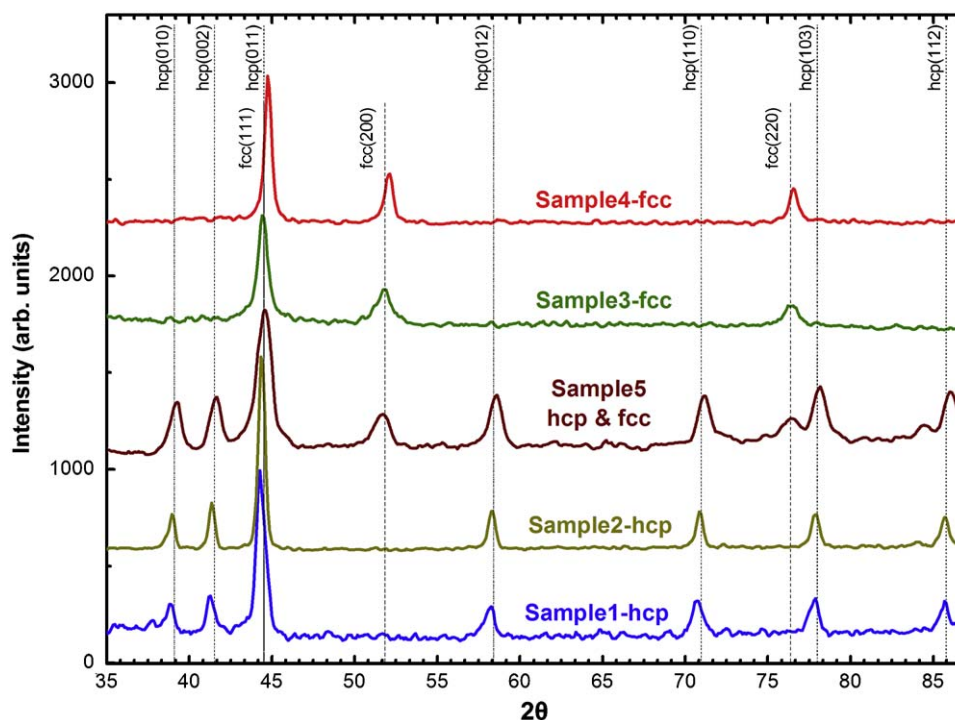


Fig. 1. X-ray powder diffraction patterns for all samples (S1–S5).

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