The influence of the starch coating on magnetic properties of nanosized cobalt ferrites obtained by different synthetic methods

Marija Šuljagić

Institut za hemiju tehnologiju i metalurgiju

Predrag Vulić

Univerzitet u Beogradu Rudarsko-Geoloski Fakultet

Dejan Jeremić

Univerzitet u Beogradu

Vladimir Pavlović

Univerzitet u Beogradu Poljoprivredni fakultet

Suzana Filipović

Institut tehnickih nauka SANU

Lukasz Kilanski

Polska Akademia Nauk Instytut Fizyki

Sabina Lewinska

Polska Akademia Nauk Instytut Fizyki

Anna Slawska-Waniewska

Polska Akademia Nauk Instytut Fizyki

Milica R. Milenković

Univerzitet u Beogradu Hemijski fakultet

Aleksandar S. Nikolić

Univerzitet u Beogradu Hemijski fakultet

Ljubica Andjelković (✉ ljubica@chem.bg.ac.rs)

Institut za hemiju tehnologiju i metalurgiju <https://orcid.org/0000-0001-5971-5383>

Research Article

Keywords: Oxide materials, Ferrimagnetism, Magnetic measurements, Nanocrystalline powders, Functionalization with starch

Posted Date: May 11th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-27272/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Materials Research Bulletin on February 1st, 2021. See the published version at <https://doi.org/10.1016/j.materresbull.2020.111117>.

Abstract

To investigate the magnetic behaviour of starch coated cobalt ferrites, five well established synthetic methods, i.e. co-precipitation, mechanochemical, ultrasonically assisted co-precipitation, microemulsion, and microwave-assisted hydrothermal syntheses were chosen for the materials' preparation. Obtained cobalt ferrites had pure single-phase spinel structures. Scanning and transmission electron microscopy analyses revealed that the morphology of samples is not uniform, and aggregation of individual particles is a dominant process in all cases. Fourier-transform infrared spectra confirmed the presence of starch in all coated samples. The unusually higher magnetization of starch-coated samples than the magnetization of their as-prepared analogs obtained by co-precipitation, ultrasonically assisted co-precipitation and microwave-assisted hydrothermal methods might be explained by the Ostwald ripening mechanism induced by coating process. On the other hand, the decrease of saturation magnetization value was noticed for starch-functionalized nanomaterials synthesized in mechanochemical and microemulsion manner, in comparison to their as-prepared analogs, showing that the size distribution of such nanoparticles is narrow and the average diameter of the grains is near critical for the Ostwald ripening process.

1. Introduction

Stable suspensions of magnetic nanoparticles (MNPs) *aka* ferrofluids, initially developed for technological applications [1–3], recently became materials with an impact in fields of analytical chemistry, biosensing, and nanomedicine [4–11]. Rapid development in the design of MNPs with desired size, morphology, chemical composition, and surface chemistry require a multidisciplinary point of view, both from chemistry associated with the challenging synthetic methods and physics utilized for the determination and optimization of their magnetic properties [12]. Magnetism presents an important prerequisite to employ nanoparticles as building blocks for different biological applications: contrast agents for magnetic resonance imaging (MRI), bio-assays using magnetic separation, internal heat sources for thermo-ablation of tumors, drug carriers with magnetic guiding capability, targeted drug release activated by an applied magnetic field and theranostics agents [5, 6, 13–16]. Functional nanoparticles in the sub-100 nm regime with controlled shape and morphology, owing mostly to their size, can penetrate cell walls, and deliver drugs for diagnostic and therapeutic purposes in an efficient manner. Moreover, regarding e.g. hyperthermia, a uniform distribution of nanoparticles determines well-controlled temperature increase in tumor tissue. Applications of MNPs in the biomedical field are limited by their biocompatibility and colloidal stability of the nanoparticles. This can be overcome by proper layering and capping using surface layers of polymers, silica, functionalized long-chain organic molecules, etc. [17–23]. Biocompatible shells can be designed to obtain an affinity to target different molecules. However, to tailor property such as surface area, particle size presents the major precondition. Literature is rife with controlled size and shape chemical preparation methods of MNPs [24–29]. Generally, the size of nanoparticles is strongly affected by boiling point of solvent [30], reaction time [31],

and annealing conditions [32, 33], while their shape is usually tuned by varying the heating rate [34], the precursor/surfactant ratio [35], the reaction time or the concentration of reagent [36, 37].

Among many magnetic materials, cobalt ferrite (CoFe_2O_4), with cubic-closest-packed inverse spinel structure, attracted great attention due to its unique magnetic, electronic, optical and physical properties, such as chemical and thermal stabilities, large magnetocrystalline anisotropy, high Curie temperature and high coercivity at room temperature. These outstanding properties made CoFe_2O_4 a promising and suitable candidate for a large variety of different medical applications [38–40]. A plethora of different synthesis procedures have been developed to produce CoFe_2O_4 nanoparticles with improved physical and chemical properties [34, 37, 41–55]. However, some preparation procedures may result in very small particles with poor magnetic properties, wide size particle distribution, non-stoichiometric ferrites and presence of non-magnetic iron oxide phases. Small sizes can somehow be eliminated by annealing over 600 °C [47]. On the other hand, possible sintering may lead to the particles' size larger than the critical size for single-domain behavior and restrict surface modification. Furthermore, the production of ferrites with pure spinel phases in some cases requires post annealing treatment [56].

In this study stoichiometric CoFe_2O_4 MNPs were synthesized by five different preparation techniques, i.e. co-precipitation, ultrasonically assisted co-precipitation, mechanochemical, microwave-assisted hydrothermal, and microemulsion syntheses. These methods were chosen, due to their fast performance, simplicity, reproducibility, and possibility of use on a mass scale. Moreover, such techniques are well-known to scientific community for the preparation of MNPs with desired performances. To obtain stable and biocompatible colloids, necessary for possible medical applications, all magnetic cores were coated with starch, strongly hydrophilic and biodegradable natural compound. Starch interacts with the surface of the MNPs through hydroxylic (R-OH) groups, resulting in a relatively weakly bonded coating provided by electrostatic interactions in a colloidal assembly [57]. The crystallinity, morphology, and chemical composition of these MNPs were studied using X-ray powder diffraction, scanning electron microscopy and Energy-dispersive X-ray spectroscopy, and transmission electron microscopy. The magnetic properties of all samples were measured and discussed. The effects of starch coating on the magnetization of CoFe_2O_4 nanoparticles were clarified, giving the rise to magnetically driven applications.

2. Materials And Methods

2.1 Materials

All chemicals (iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 98%), Cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 98%), Sodium hydroxide (NaOH, > 97%), Cetyltrimethylammonium bromide (CTAB, > 98%), n-butanol (99.8%), n-hexanol (> 99%), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, > 99.95), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, > 99.99), ammonium hydroxide solution (28% NH_3 in water), absolute

ethanol and soluble starch) were obtained by Sigma-Aldrich (p.a. quality), and used without additional purification. Deionized water was used in these experiments.

2.2 Preparation procedure

2.2.1 Co-precipitation synthesis

The samples were synthesized using 0.02 mol Fe^{3+} and 0.01 mol Co^{2+} chlorides as precursors, by dissolving them in 50 mL of deionized water and then heated up to the boiling. To ensure complete precipitation of cobalt and iron cations the excess of 1M NaOH solution was rapidly added with constant stirring. The appearance of black precipitate was noticed and pH value of the solution was 11. The reaction mixture was refluxed for 1 hour. The mixture was cooled to room temperature and filtered. The precipitate was washed with distilled water until the excess of hydroxide was completely removed (neutral pH value) and dried at 100 °C for 2 hours. Furthermore, the powder was divided into two equal parts. First part was pulverized in an agate mortar and annealed in an electrical furnace with a heating rate of 10 °C/min at $T = 450$ °C for 1 hour. The second part was transferred to the planetary mill.

2.2.2 Mechanochemical synthesis

Mechanochemical treatment was performed in a planetary ball mill (Retsch PM100CM). A hardened-steel vial (500 cm³ volume) filled with 10 hardened-steel balls (8 mm in diameter) was used as the milling medium. The powder prepared by co-precipitation method was ball-milled for 10 h at 500 rpm in closed hardened steel containers, with a ball-to-sample mass ratio 20 : 1. The angular velocity of the supporting disc and vial was 32.2 and 40.3 rad s⁻¹, respectively. The intensity of milling corresponded to an acceleration of about 10 times the gravitational acceleration.

2.2.3 Ultrasonically assisted co-precipitation synthesis

Solutions of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ were mixed in their stoichiometric ratio. The concentrations of Fe^{3+} and Co^{2+} was 0.4 M and 0.2 M, respectively. The final volume of solution was 50 mL. To this, excess of 1M NaOH was rapidly added with constant stirring. The pH of the solution was maintained at 11. The mixture was then heated at 80 °C and ultrasonically treated for about 1 hour. The precipitated particles were then washed several times with deionized water to remove the hydroxide residues and other impurities. The precipitate was further dried at 80 °C, followed by pulverization in the agate mortar, and annealed in the electrical furnace as the sample obtained by co-precipitation (Sect. 2.2.1).

2.2.4 Microemulsion synthesis

A microemulsion system with CTAB as the surfactant, n-butanol as the cosurfactant, n-hexanol as the oil phase and an aqueous solution as the water phase was chosen. Microemulsion contained 15 wt% of hexanol, 45 wt% of the aqueous solution and surfactant to co-surfactant ratio was 60/40. Two microemulsions with identical compositions but different aqueous phases were taken. The first microemulsion contained aqueous solutions of a stoichiometric amount of Fe^{3+} and Co^{2+} nitrates, whereas the second microemulsion contained an aqueous solution of the precipitation agent ammonium

hydroxide. These two microemulsions were then mixed under constant stirring and heated for 1 hour at 90 °C. The pH value after precipitation was about 11. The microemulsion with product nanoparticles was mixed with a water/ethanol mixture and precipitated by centrifuging. Finally, the precipitate was washed with absolute ethanol to remove any oil and surfactant residues from the particles and dried at 70 °C. The precipitate was pulverized in the agate mortar and annealed in the electrical furnace under the conditions provided in Sect. 2.2.1.

2.2.5 Microwave-assisted hydrothermal synthesis

Stoichiometric amounts of chloride salts of Fe^{3+} and Co^{2+} necessary to prepare 1.5 g of CoFe_2O_4 were dissolved in deionized water. Afterwards, the small excess of ammonium hydroxide was added. The pH value was about 10. The overall volume of the mixture was divided into seven vessels each with a volume of 100 mL. Each vessel contained 50 mL of the mixture. The vessels were placed in an HPR-1000/10S high pressure segmented rotor and heated in the microwave digester ETHOS 1, Advanced Microwave Digestion System, MILESTONE, Italy. The power of microwave irradiation was set in the range of 0-1000 W, with linear heating of the mixture at 20 °C/min. The mixture was then heated at 200 °C for 20 minutes at a maximum pressure of 100 bars. Subsequently, vessels were cooled in air. The prepared particles were separated from the solution with the support of an external permanent magnet. The precipitate was then washed several times with deionized water to remove an excess of chlorides. The synthesized nanoparticles were dried at 70 °C for one day. After drying, the residue was pulverized in the agate mortar.

2.2.6 Functionalization with starch

With the aid of ultrasound, 0.5 g of CoFe_2O_4 powders were dispersed in deionized water (20 mL). 2.5 g of starch was dissolved in boiling water and 200 mL of 2 M NaOH solution was prepared. Then, starch solutions and ferrite dispersions were mixed and added dropwise in hydroxide solutions. The obtained mixtures were ultrasonically treated for 1 h at 80 °C. Afterwards, samples were cooled to room temperature and washed with deionized water to remove an excess of starch and hydroxide. The samples were dried for 48 hours at room temperature.

2.3 Characterizations

XRPD patterns for all of the samples were collected using a Rigaku SmartLab automated powder X-ray diffractometer with $\text{Cu K}\alpha_{1,2}$ ($\lambda = 1.54059 \text{ \AA}$) radiation ($U = 40 \text{ kV}$, $I = 30 \text{ mA}$) equipped with D/teX Ultra 250 stripped 1D detector in the XRF reduction mode. The diffraction angle range was 15–90 °2 θ with a step of 0.01 ° at a scan speed of 2 °/min. Structural and microstructural investigation of all samples (cobalt ferrites and starch-coated cobalt ferrites) was conducted by the Rietveld method, as implemented in dedicated Rigaku PDXL2.0 software and based on fundamental parameters approach (FPA) [58].

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) analyses were performed with a JEOL JSM-6610LV scanning electron microscope. EDS analyses were conducted in the area of $1 \times 10^4 \text{ }\mu\text{m}^2$ per sample. Transmission electron microscopy (TEM) analysis was performed on the

JEOL JEM-1400 Plus Electron microscope, with a voltage of 120 kV and LaB6 filament, at different magnifications appropriate for observation of aggregation details.

The Fourier transform IR (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR instrument (Thermo Scientific), in the ranges of 4000–400 cm⁻¹ using the ATR technique with a Smart Orbit accessory (diamond crystal).

Magnetic measurements were performed by commercial Quantum Design Physical Property Measurement System (PPMS) with the 9 T superconductive magnet using a vibrating sample magnetometer (VSM) option. Temperature dependences of the magnetization, $M(T)$, were measured upon heating in zero-field cooled (ZFC) and field-cooled (FC) regime at 100 Oe from 5 to 300 K. Hysteresis loops, $M(H)$, were measured at 300 K in the field range ± 9 T.

3. Results And Discussion

The X-ray powder patterns of samples prepared by five different synthesis routes are shown in Figure 1. The diffractions maxima present in XRPD patterns were identified by ICDD PDF2 file number 22-1086. It is obvious that for both type of samples, as-prepared and coated, the single spinel phase is present. The formation of pure CoFe₂O₄ is confirmed in all cases with no detectable residual phase of hematite. The XRPD patterns show peaks with considerable broadening, indicating the small crystallite size of the ferrite powders. The calculated values of unit cell parameter (Å), volume (Å³), crystallite size (Å) and microstrain (%) of prepared particles are given in Table 1. The unit cell parameters are comparable to the values reported in the literature [59]. The unit cell volume and unit cell parameters are the largest for the mechanochemically prepared CoFe₂O₄. For as-prepared samples, particles prepared with aid of the ultrasound have the smallest value of crystallite size, while the crystallites obtained by microemulsion method are the largest. It can be seen that for the same annealing conditions the crystallite size samples slightly differ from each other, which reflects the strong affection of the synthesis method. The crystallite size is related to the relative interdependence between the nucleation and growth steps, and it is strongly influenced by the preparation method. This indicates that the nucleation rate was higher than the growth rate in the ultrasonically treated sample compared to the other annealed powders. In starch-coated samples the crystallite size slightly increases. Microstrain values for uncoated and corresponding coated samples are similar. Among all investigated powders, microstrain value is the smallest for the CoFe₂O₄ prepared in microemulsion manner, due to the lowest temperature of preparation.

Table 1. Unit cell parameters (Å), volumes (Å³) and microstructural parameters for the investigated cobalt ferrites

CoFe ₂ O ₄ prepared by	Unit cell parameter (Å)	Volume (Å ³)	Crystallite Size (nm)	Microstrain (%)
Co-precipitation method	8.3723(5)	586.98(7)	12.0(2)	0.32(6)
Co-precipitation method*	8.3738(5)	587.17(7)	12.1(2)	0.44(3)
Mechanochemical method	8.3845(5)	589.42(7)	11.3(2)	0.39(5)
Mechanochemical method*	8.3888(4)	590.34(6)	12.5(1)	0.37(2)
Ultrasonically assisted co-precipitation method	8.3558(6)	583.40(8)	11.9(1)	0.54(2)
Ultrasonically assisted co-precipitation method*	8.3616(5)	584.61(6)	13.9(2)	0.37(4)
Microemulsion method	8.3610(4)	584.49(5)	12.8(2)	0.15(4)
Microemulsion method*	8.3628(4)	584.87(5)	14.3(1)	0.11(5)
Microwave assisted hydrothermal method	8.3738(4)	587.18(6)	12.5(2)	0.41(4)
Microwave assisted hydrothermal method*	8.3785(5)	588.17(6)	15.0(1)	0.52(2)

*starch-coated

In all investigated samples, EDS analyses corroborate divalent cobalt and trivalent iron stoichiometric ratio 1:2. SEM analysis was performed to visualize the morphology of the synthesized magnetic nanoparticles. According to the SEM results (Figure 2), it is visible that the synthesized particles have significant tendency of agglomeration due to their ferrimagnetic nature. Further, it was noticed presence of smaller agglomerates 150-400 nm in size and bigger with dimensions around 0.7-1.5 µm. In order to obtain more detail picture of the synthesized powders' microstructure, TEM was performed. Recorded TEM micrographs are presented in Figure 3. General observation is that morphology of samples is not uniform, and aggregations of individual particles are dominant process in all monitored samples. Two kinds of particles are noticed in presented micrographs, bigger polygonal and smaller one with almost spherical shape. The polygonal particles are larger than 20 nm, while smaller are in range 10-20 nm. The structure of smaller particles gravitates to amorphous, in contrast to polygonal ones. This could be explained by mechanism of crystalline CoFe₂O₄ formation. In first step of chemical reaction amorphous CoFe₂O₄ was formed, and during heat treatment reaction propagates along with crystallization and grain growth. It was shown in literature that for this type of materials, throughout grain growth changes in morphology are observed [60]. From TEM images of starch-coated powders (right side of Figure 3) encapsulation of individual particles) cannot be noticed. Thus, the conclusions about changes in particle size cannot be made.

FT-IR spectra of as-prepared and coated particles, taken in the range of 4000 to 400 cm^{-1} , are presented in Figure 4. The exact wavenumbers and band assignments are given in Table 2. The fingerprint region of FT-IR spectra showed M–O (M = Co, Fe) stretching modes of spinel ferrites, i.e. two characteristic vibrational modes for spinel structure about 570 cm^{-1} and 420 cm^{-1} are present in all investigated samples. The strong band corroborated stretching vibrations of Fe^{3+} ion at a tetrahedral site ($\text{Fe}_{\text{tetra}}\text{--O}$), while the band of weaker intensity originated from Co^{2+} vibrations at an octahedral site ($\text{Co}_{\text{octa}}\text{--O}$). Free or absorbed water in samples caused the appearance of two peaks near 3360 and 1630 cm^{-1} . FT-IR spectra given in Figure 4b confirmed the attachment of starch moieties, i.e. five bands around 2930, 1450, 1340, 1000 and 920 cm^{-1} typical for starch can be found [21, 61]. The weak band about 2930 cm^{-1} can be assigned to stretching vibrations of --CH_2 and --CH groups while the bands near 1450 and 1340 cm^{-1} are connected to their bending vibrations. The band corresponding to 1000 cm^{-1} represents C–OH stretching mode. The absorption peak at 920 cm^{-1} is due to stretching vibrations of glycosidic linkages (C–O–C) [21]. Therefore, FT-IR spectra confirmed the presence of starch in all investigated coated samples.

Table 2. IR assignment for CoFe_2O_4 particles prepared by: co-precipitation method (A), mechanochemical method (B), ultrasonically assisted co-precipitation method (C), microemulsion method (D) and microwave assisted hydrothermal method (E).

<i>Wavenumbers for uncoated particles (cm⁻¹)</i>					<i>Assignments</i>
A	B	C	D	E	
3367	3372	3361	3388	3361	Stretching vibrations of water
1635	1640	1630	1613	1633	Bending vibrations of water
558	574	580	563	559	Fe _{tetra} -O
417	423	428	439	428	Co _{octa} -O
<i>Wavenumbers for coated particles (cm⁻¹)</i>					
3363	3359	3339	3329	3332	Hydrogen bonded OH stretching
2931	2936	2920	2941	2931	CH and CH ₂ stretching
1636	1628	1574	1629	1633	Bending vibrations of water
1454	1460	1461	1421	1465	CH ₂ bending in plane
1351	1340	1335	1381	1362	CH bending in plane
999	996	1025	1039	1020	COH stretching
922	912	925	927	925	C-O-C stretching
580	576	573	558	575	Fe _{tetra} -O
430	426	400	428	412	Co _{octa} -O

Figure 5 shows the temperature (left side) and magnetic field (right side) dependences of the magnetization, M , for both, as-prepared and starch-coated CoFe_2O_4 samples measured using PPMS.

Left part of the Figure 5 presents the temperature dependencies of the magnetization measured at zero-field-cooled (ZFC) and field-cooled (FC) regime at the applied field of 100 Oe for all investigated samples. All measured ZFC-FC relations have similar curvature. The ZFC relations do not exhibit any extrema and the magnetization increases with the temperature from 5 to 300 K. All FC curves are nearly constant over the above-mentioned temperature range. With the introduction of the starch, changes of the magnetization values of the ZFC-FC relations are observed with respect to the uncoated samples. However, these changes are not systematic from sample to sample. In the case of samples prepared using co-precipitation and ultrasonically assisted co-precipitation methods, the $M(T)$ curves showed higher values for starch-coated nanoparticles. In contrast, for the CoFe_2O_4 nanoparticles prepared using mechanochemical and microemulsion methods the $M(T)$ curves for the as-prepared samples have larger values than for the starch-coated samples. It should be also noted that the smallest differences between

the $M(T)$ curves for as-prepared and coated sample were observed for samples obtained with the microwave assisted hydrothermal method. In Figure 5 is also well visible that for the starch-coated sample prepared by the microemulsion method the ZFC curve obtained negatives values below 200 K.

On the right side of Figure 5, a set of results of magnetization measurements as a function of the magnetic field obtained at $T = 300$ K for both, as-prepared and starch-coated CoFe_2O_4 nanoparticle samples, is presented. All the $M(H)$ curves exhibit different and non-zero coercive field values, H_C , and different values of the magnetization at 90 kOe, here called the M_S (Table 3). As same as for ZFC-FC relations, M_S values after the starch coating do not exhibit systematic changes. For the samples prepared by co-precipitation, ultrasonically assisted co-precipitation and microwave assisted hydrothermal methods M_S increased by ca. 5-7% compared to the samples without coating. For the two remaining samples, starch coating caused the reduction of M_S at the level near 10 and 18%.

Table 3. The magnetization (M_S) at 90 kOe and non-zero coercive field (H_C) values for all investigated samples

CoFe ₂ O ₄ prepared by	As-prepared		Starch-coated	
	M_S (emu/g)	H_C (Oe)	M_S (emu/g)	H_C (emu/g)
Co-precipitation method	66	329	70	231
Mechanochemical method	72	407	59	400
Ultrasonically assisted co-precipitation method	61	291	66	266
Microemulsion method	70	1206	63	1219
Microwave assisted hydrothermal method	70	723	73	702

In Figure 5, $M/M_S(H)$ relations are also plotted. It should be noted that the best overlapping between hysteresis loops measured for pair of as-prepared and coated samples is observed for samples prepared by the microemulsion method. Also, for the pairs of the samples made by mechanochemical and microwave assisted hydrothermal methods the curvature differences in $M/M_S(H)$ are very slight but noticeable below 20 kOe. The most significant variation in curvature of $M/M_S(H)$ relations for as-prepared and coated samples is well visible for materials obtained by co-precipitation and ultrasonically assisted co-precipitation method – loops for samples without and with starch do not overlap below 30 kOe.

Comparable ZFC-FC relations (without visible maximum in ZFC curve and nearly constant in the temperature value of FC curve up to 300K) were observed earlier for cobalt ferrite nanoparticles [52, 62]. Kim et al, explained registered ZFC relation based on Mössbauer spectra for 15 nm CoFe_2O_4 nanoparticles synthesized by temperature-controlled co-precipitation method [62]. Authors predicted that

their sample up to 550°C is composed of superparamagnetic and ferromagnetic fraction, thus the maximum in ZFC curve is not registered and non-zero H_C at 300K is observed [62]. However, this explanation is hard to relate with our results. As it can be seen from Figures 2 and 3, synthesized CoFe_2O_4 nanoparticles with and without starch coating are agglomerated systems. In such systems grains are very close to each other and it is expected that interaction between them is significant and has the influence on the macroscopic magnetic properties [63]. Taking into account $M(T)$ data gathered in Figure 5, this allow us to state the presence of magnetic interactions between the magnetic nanoparticles in all investigated samples.

The obtained M_S values (at 300 K) for all discussed samples are lower than 80 emu/g, expected for bulk CoFe_2O_4 [64]. Observed reduction of saturation magnetization with regard to the bulk values is probably related to the near-surface layer, where the disorder of the magnetic moments is possible [63, 65, 66]. What is noteworthy, for samples prepared using mechanochemical and microemulsion methods, observed decrease of M_S after the starch coating is consistent with theoretical prediction and literature [67, 68]. It is well known that starch is a diamagnetic material, therefore covering CoFe_2O_4 nanoparticles with it should lead to a decrease in magnetization per mass unit. The contribution of diamagnetic starch is also well visible for the starch-coated sample prepared by the microemulsion method where the ZFC curve obtained negatives values below 200 K.

For the samples prepared by co-precipitation, ultrasonically assisted co-precipitation and microwave assisted hydrothermal methods M_S values registered after starch coating gave unexpected results – the increase of M_S . It is quite possible that ultrasound used during the coating procedure can destroy smaller aggregates in the synthesized samples and rearrangement of the particles by Ostwald mechanism (also called coarsening) can occur. There is no direct but possible correlation between Ostwald ripening process and M_S value. In the Ostwald ripening process larger particles enhance their diameters at the expense of smaller ones, resulting in the shift of the particle distribution to higher diameter values. This mechanism is related to thermodynamic stability of the system, i.e. smaller particles have higher solubility then larger ones [69, 70]. It is known that in nanoparticles' systems M_S values increase with the diameter of particles [47, 71, 72]. Thus, if during the starch coating process, the average diameter of nanoparticles increases by Ostwald mechanism, the enhancement of M_S value after coating becomes possible. It should be noted that the potential presence of coarsening process for samples prepared by co-precipitation, ultrasonically assisted co-precipitation and microwave assisted hydrothermal methods do not exclude the existence of the starch coating. Most likely, the increase of M_S value induced by the enhancement of average particles' dimensions in these three samples is more significant than the reduction of M_S value after the functionalization of nanoparticles. The Ostwald ripening process takes place only if in the system exist particles with diameter below critical radius. This critical radius is connected with solubility of the particles. If the particles have dimensions equal or above critical diameter the process does not take place. In this context, we suppose that for the samples made by mechanochemical and microemulsion methods the size distribution of nanoparticles is narrow and the

average diameter of the grains is near critical for Ostwald ripening process, thus the influence of the coarsening is not so significant as in the case of three other samples [70].

4. Conclusion

To demonstrate how CoFe_2O_4 structures and ultrasonically-assisted starch coating are intertwined with the resulting magnetic properties, five different synthesis methods were performed. The XRPD patterns for all investigated samples revealed characteristic peaks for the pure spinel structure. According to the SEM and TEM data, the presence of highly agglomerated nanometric CoFe_2O_4 powders was confirmed. The FT-IR results clearly indicated the presence of starch. Attention should be paid to the fact that examined samples may be divided into two main groups. Starch functionalization of the samples prepared by co-precipitation, ultrasonically assisted co-precipitation and microwave assisted hydrothermal methods resulted in the slight increase of M_S value. The curvature of hysteresis loops changed after coating process, especially for the samples obtained by co-precipitation and ultrasonically assisted co-precipitation methods, opening new perspectives for –OH based coating of nanoparticles for application in biomedicine. These unexpected magnetic properties are linked to the Ostwald ripening process, i.e. diffusion of smaller particles onto larger ones probably caused by ultrasound assistance during the coating procedure. It should be noted that this hypothesis does not exclude the existence of the starch in samples prepared by co-precipitation, ultrasonically assisted co-precipitation, and microwave assisted hydrothermal methods.

In the second group, where samples prepared by mechanochemical and microemulsion methods can be assigned, the theoretically predicted decrease of M_S value was registered. Observed decrease of M_S values after the starch coating is a consequence of the reduction of content of the magnetic component for these two samples. However, the magnetic properties of coated nanoparticles synthesized in mechanochemical and microemulsion manner, as well as their narrow size distribution gives us the confidence for their further medical application.

Finally, the magnetic properties of ferrite-based nanomaterials, dependent on the physical parameters, such as size, shape, composition, and core-shell architecture, can be selectively and judiciously tuned by the proper choice of the synthesis route.

Declarations

Acknowledgements

This work was financially supported by the Serbian Ministry of Education, Science and Technological Development (Grant No. 451-03-68/2020-14/200026). Ljubica Andjelković acknowledges “Startup for Science, Serbia” 2017/18.

This paper is dedicated to the memory of our friend and colleague, Predrag Vulić.

References

1. Jeong U, Teng X, Wang Y, et al. Superparamagnetic Colloids: Controlled Synthesis and Niche Applications. *Adv Mater.* 2007;19:33–60.
2. Lu AH, Salabas EL, Schüth F. Magnetic Nanoparticles: Synthesis, Protection, Functionalization, and Application. *Angew Chem Int Ed.* 2007;46:1222–44.
3. Park BJ, Fang FF, Choi HJ. Magnetorheology: materials and application. *Soft Matter.* 2010;6:5246–53.
4. Pankhurst QA, Connolly J, Jones SK, Dobson J. Applications of magnetic nanoparticles in biomedicine. *J Phys D.* 2003;36:R167.
5. Corot C, Robert P, Idée JM, Port M. Recent advances in iron oxide nanocrystal technology for medical imaging. *Adv Drug Deliv Rev.* 2006;58:1471–504.
6. Hervault A, Thanh NTK. Magnetic nanoparticle-based therapeutic agents for thermo-chemotherapy treatment of cancer. *Nanoscale.* 2014;6:11553–73.
7. Tran N, Webster TJ. Magnetic nanoparticles: biomedical applications and challenges. *J Mater Chem.* 2010;20:8760–7.
8. Durán JDG, Arias JL, Gallardo V, Delgado AV. Magnetic Colloids As Drug Vehicles. *J Pharm Sci.* 2008;97:2948–83.
9. Chen Q, Li D, Lin J, et al. Simultaneous Separation and Washing of Nonmagnetic Particles in an Inertial Ferrofluid/Water Coflow. *Anal Chem.* 2017;89:6915–20.
10. Yamaguchi D, Furukawa K, Takasuga M, Watanabe K. A Magnetic Carbon Sorbent for Radioactive Material from the Fukushima Nuclear Accident. *Sci Rep.* 2014;4:6053.
11. Mohammed L, Gomaa HG, Ragab D, Zhu J. Magnetic nanoparticles for environmental and biomedical applications: A review. *Particuology.* 2017;30:1–14.
12. Kolhatkar AG, Jamison AC, Litvinov D, et al. Tuning the Magnetic Properties of Nanoparticles. *Int J Mol Sci.* 2013;14:15977–6009.
13. Amstad E, Zurcher S, Mashaghi A, et al. Surface Functionalization of Single Superparamagnetic Iron Oxide Nanoparticles for Targeted Magnetic Resonance Imaging. *Small.* 2009;5:1334–42.
14. Chao-Ming F, Yuh-Feng W, Yu-Feng G, et al. In vivo bio-distribution of intravenously injected Tc-99 m labeled ferrite nanoparticles bounded with biocompatible medicals. *IEEE Trans Magn.* 2005;41:4120–2.
15. Chourpa I, Douziech-Eyrolles L, Ngaboni-Okassa L, et al. Molecular composition of iron oxide nanoparticles, precursors for magnetic drug targeting, as characterized by confocal Raman microspectroscopy. *Analyst.* 2005;130:1395–403.
16. Laurent S, Dutz S, Häfeli UO, Mahmoudi M. Magnetic fluid hyperthermia: Focus on superparamagnetic iron oxide nanoparticles. *Adv Colloid Interface Sci.* 2011;166:8–23.

17. Goloverda G, Jackson B, Kidd C, Kolesnichenko V. Synthesis of ultrasmall magnetic iron oxide nanoparticles and study of their colloid and surface chemistry. *J Magn Magn Mater*. 2009;321:1372–6.
18. Gupta AK, Gupta M. Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomaterials*. 2005;26:3995–4021.
19. Sun J, Zhou S, Hou P, et al. Synthesis and characterization of biocompatible Fe₃O₄ nanoparticles. *J Biomed Mater Res A*. 2007;80A:333–41.
20. Tadmor R, Rosensweig RE, Frey J, Klein J. Resolving the Puzzle of Ferrofluid Dispersants. *Langmuir*. 2000;16:9117–20.
21. Kim DH, Kim KN, Kim KM, Lee YK. Targeting to carcinoma cells with chitosan- and starch-coated magnetic nanoparticles for magnetic hyperthermia. *J Biomed Mater Res A*. 2009;88A:1–11.
22. Cole AJ, David AE, Wang J, et al. Polyethylene glycol modified, cross-linked starch-coated iron oxide nanoparticles for enhanced magnetic tumor targeting. *Biomaterials*. 2011;32:2183–93.
23. Kim DK, Mikhaylova M, Wang FH, et al. Starch-Coated Superparamagnetic Nanoparticles as MR Contrast Agents. *Chem Mater* 2003, 15: 4343–4351.
24. Lu LT, Dung NT, Tung LD, et al. Synthesis of magnetic cobalt ferrite nanoparticles with controlled morphology, monodispersity and composition: the influence of solvent, surfactant, reductant and synthetic conditions. *Nanoscale*. 2015;7:19596–610.
25. Chen YX, Chen SP, Zhou ZY, et al. Tuning the Shape and Catalytic Activity of Fe Nanocrystals from Rhombic Dodecahedra and Tetragonal Bipyramids to Cubes by Electrochemistry. *J Am Chem Soc*. 2009;131:10860–2.
26. Xiaohe L, Guanzhou Q, Xingguo L. Shape-controlled synthesis and properties of uniform spinel cobalt oxide nanocubes. *Nanotechnology*. 2005;16:3035.
27. Andrade ÂL, Valente MA, Ferreira JMF, Fabris JD. Preparation of size-controlled nanoparticles of magnetite. *J Magn Magn Mater*. 2012;324:1753–7.
28. Wang SB, Min YL, Yu SH. Synthesis and Magnetic Properties of Uniform Hematite Nanocubes. *J Phys Chem C*. 2007;111:3551–4.
29. Baaziz W, Pichon BP, Liu Y, et al. Tuning of Synthesis Conditions by Thermal Decomposition toward Core–Shell Co_xFe_{1–x}O@Co_yFe_{3–y}O₄ and CoFe₂O₄ Nanoparticles with Spherical and Cubic Shapes. *Chem Mater*. 2014;26:5063–73.
30. Kovalenko MV, Bodnarchuk MI, Lechner RT, et al. Fatty Acid Salts as Stabilizers in Size- and Shape-Controlled Nanocrystal Synthesis: The Case of Inverse Spinel Iron Oxide. *J Am Chem Soc*. 2007;129:6352–3.
31. Yang H, Ogawa T, Hasegawa D, Takahashi M. Synthesis and magnetic properties of monodisperse magnetite nanocubes. *J Appl Phys*. 2008;103:07D526.
32. Hu XC, Capobianchi A, Gallagher R, Hadjipanayis GC. Influence of ball milling and annealing conditions on the properties of L10 FePt nanoparticles fabricated by a new green chemical synthesis

- method. *J Appl Phys*. 2014;115:17A732.
33. Yeshchenko OA, Dmitruk IM, Dmytruk AM, Alexeenko AA. Influence of annealing conditions on size and optical properties of copper nanoparticles embedded in silica matrix. *Mater Sci Eng B Solid State Mater Adv Technol*. 2007;137:247–54.
 34. Song Q, Zhang ZJ. Shape Control and Associated Magnetic Properties of Spinel Cobalt Ferrite Nanocrystals. *J Am Chem Soc*. 2004;126:6164–8.
 35. Zeng H, Rice PM, Wang SX, Sun S. Shape-Controlled Synthesis and Shape-Induced Texture of MnFe_2O_4 Nanoparticles. *J Am Chem Soc*. 2004;126:11458–9.
 36. Salazar-Alvarez G, Qin J, Šepelák V, et al. Cubic versus Spherical Magnetic Nanoparticles: The Role of Surface Anisotropy. *J Am Chem Soc*. 2008;130:13234–9.
 37. Bao N, Shen L, Padhan P, Gupta A. Self-assembly and magnetic properties of shape-controlled monodisperse CoFe_2O_4 nanocrystals. *Appl Phys Lett*. 2008;92:173101.
 38. Kim DH, Nikles DE, Johnson DT, Brazel CS. Heat generation of aqueously dispersed CoFe_2O_4 nanoparticles as heating agents for magnetically activated drug delivery and hyperthermia. *J Magn Magn Mater*. 2008;320:2390–6.
 39. Lee SW, Bae S, Takemura Y, et al. Self-heating characteristics of cobalt ferrite nanoparticles for hyperthermia application. *J Magn Magn Mater*. 2007;310:2868–70.
 40. Joshi HM, Lin YP, Aslam M, et al. Effects of Shape and Size of Cobalt Ferrite Nanostructures on Their MRI Contrast and Thermal Activation. *J Phys Chem C*. 2009;113:17761–7.
 41. Cheng F, Peng Z, Liao C, et al. Chemical synthesis and magnetic study of nanocrystalline thin films of cobalt spinel ferrites. *Solid State Commun*. 1998;107:471–6.
 42. Shi Y, Ding J, Yin H. CoFe_2O_4 nanoparticles prepared by the mechanochemical method. *J Alloys Compd*. 2000;308:290–5.
 43. Liu Q, Sun J, Long H, et al. Hydrothermal synthesis of CoFe_2O_4 nanoplatelets and nanoparticles. *Mater Chem Phys*. 2008;108:269–73.
 44. Sun S, Zeng H, Robinson DB, et al. Monodisperse MFe_2O_4 (M = Fe, Co, Mn) Nanoparticles. *J Am Chem Soc*. 2004;126:273–9.
 45. Mathew DS, Juang RS. An overview of the structure and magnetism of spinel ferrite nanoparticles and their synthesis in microemulsions. *Chem Eng J*. 2007;129:51–65.
 46. Bao N, Shen L, Wang Y, et al. A Facile Thermolysis Route to Monodisperse Ferrite Nanocrystals. *J Am Chem Soc*. 2007;129:12374–5.
 47. Maaz K, Mumtaz A, Hasanain SK, Ceylan A. Synthesis and magnetic properties of cobalt ferrite (CoFe_2O_4) nanoparticles prepared by wet chemical route. *J Magn Magn Mater*. 2007;308:289–95.
 48. Bao N, Shen L, An W, et al. Formation Mechanism and Shape Control of Monodisperse Magnetic CoFe_2O_4 Nanocrystals. *Chem Mater*. 2009;21:3458–68.

49. Bao N, Shen L, Wang YHA, et al. Controlled Growth of Monodisperse Self-Supported Superparamagnetic Nanostructures of Spherical and Rod-Like CoFe_2O_4 Nanocrystals. *J Am Chem Soc.* 2009;31:12900–1.
50. Liu XM, Fu SY, Zhu LP. High-yield synthesis and characterization of monodisperse sub-microsized CoFe_2O_4 octahedra. *J Solid State Chem.* 2007;180:461–6.
51. Baldi G, Bonacchi D, Innocenti C, et al. Cobalt ferrite nanoparticles: The control of the particle size and surface state and their effects on magnetic properties. *J Magn Magn Mater.* 2007;311:10–6.
52. Ognjanović M, Dojčinović B, Fabián M, et al. Microwave assisted hydrothermal synthesis of $(\text{Fe,Co})_3\text{O}_4$ nanoparticles in the presence of surfactants and effects of Co/Fe ratio on microstructure and magnetism. *Ceram Int.* 2018;44:13967–72.
53. Abbas M, Parvatheeswara Rao B, Nazrul Islam M, et al. Size-controlled high magnetization CoFe_2O_4 nanospheres and nanocubes using rapid one-pot sonochemical technique. *Ceram Int.* 2014;40:3269–76.
54. Zhang Y, Yang Z, Yin D, et al. Composition and magnetic properties of cobalt ferrite nano-particles prepared by the co-precipitation method. *J Magn Magn Mater.* 2010;322:3470–5.
55. Pedrosa FJ, Rial J, Golasinski KM, et al. Tunable nanocrystalline CoFe_2O_4 isotropic powders obtained by co-precipitation and ultrafast ball milling for permanent magnet applications. *RSC Adv.* 2016;6:87282–7.
56. Ai L, Jiang J. Influence of annealing temperature on the formation, microstructure and magnetic properties of spinel nanocrystalline cobalt ferrites. *Curr Appl Phys.* 2010;10:284–8.
57. Vasilakaki M, Ntallis N, Yaacoub N, et al. Optimising the magnetic performance of Co ferrite nanoparticles via organic ligand capping. *Nanoscale.* 2018;10:21244–53.
58. Cheary RW, Coelho A. A fundamental parameters approach to X-ray line-profile fitting. *J Appl Crystallogr.* 1992;25:109–21.
59. Houshiar M, Zebhi F, Razi ZJ, et al. Synthesis of cobalt ferrite (CoFe_2O_4) nanoparticles using combustion, coprecipitation, and precipitation methods: A comparison study of size, structural, and magnetic properties. *J Magn Magn Mater.* 2014;371:43–8.
60. Phua LX, Xu F, Ma YG, Ong CK. Structure and magnetic characterizations of cobalt ferrite films prepared by spray pyrolysis. *Thin Solid Films.* 2009;517:5858–61.
61. Warren FJ, Gidley MJ, Flanagan BM. Infrared spectroscopy as a tool to characterise starch ordered structure—a joint FTIR–ATR, NMR, XRD and DSC study. *Carbohydr Polym.* 2016;139:35–42.
62. Kim YI, Kim D, Lee CS. Synthesis and characterization of CoFe_2O_4 magnetic nanoparticles prepared by temperature-controlled coprecipitation method. *Physica B: Condens Matter.* 2003;337:42–51.
63. Knobel M, Nunes WC, Socolovsky LM, et al. Superparamagnetism and Other Magnetic Features in Granular Materials: A Review on Ideal and Real Systems. *J Nanosci Nanotechnol.* 2008;8:2836–57.
64. Cullity BD, Graham CD. *Introduction to Magnetic Materials*. Wiley-IEEE Press, 2008.

65. Batlle X, Labarta A. Finite-size effects in fine particles: magnetic and transport properties. *J Phys D*. 2002;35:R15–42.
66. Linderöth S, Hendriksen PV, Bødker F, et al. On spin-canting in maghemite particles. *J Appl Phys*. 1994;75:6583–5.
67. Covaliu CI, Berger D, Matei C, et al. Magnetic nanoparticles coated with polysaccharide polymers for potential biomedical applications. *J Nanoparticle Res*. 2011;13:6169–80.
68. Dung TT, Danh TM, Hoa LTM, et al. Structural and magnetic properties of starch-coated magnetite nanoparticles. *J Exp Nanosci*. 2009;4:259–67.
69. Ayyappan S, Philip J, Raj B. Effect of Digestion Time on Size and Magnetic Properties of Spinel CoFe_2O_4 Nanoparticles. *J Phys Chem C*. 2009;113:590–6.
70. Finsky R. On the Critical Radius in Ostwald Ripening. *Langmuir*. 2004;20:2975–6.
71. Lu HM, Zheng WT, Jiang Q. Saturation magnetization of ferromagnetic and ferrimagnetic nanocrystals at room temperature. *J Phys D*. 2007;40:320–5.
72. Sharifi Dehsari H, Asadi K. Impact of Stoichiometry and Size on the Magnetic Properties of Cobalt Ferrite Nanoparticles. *J Phys Chem C*. 2018;122:29106–21.

Figures

Figure 1

Collected XRPD patterns of uncoated and starch-coated cobalt ferrites. CoFe_2O_4 prepared by a) co-precipitation method, b) co-precipitation method/starch coating, c) mechanochemical method, d) mechanochemical method/starch coating, e) ultrasonically assisted co-precipitation method, f) ultrasonically assisted co-precipitation method/starch coating, g) microemulsion method, h)

microemulsion/starch coating, i) microwave-assisted hydrothermal method, j) microwave-assisted hydrothermal method/starch coating.

Figure 2

SEM analysis of the synthesized cobalt ferrites.

Figure 3

TEM analysis of the synthesized cobalt ferrites.

Figure 4

FT-IR spectra of a) as-prepared and b) starch-coated CoFe₂O₄ particles prepared by: co-precipitation method (black), mechanochemical method (blue), ultrasonically assisted co-precipitation method (red), microemulsion method (green) and microwave-assisted hydrothermal method (purple).

Figure 5

Results of the magnetization measurements obtained for the synthesized samples including (i) magnetization as a function of temperature measured at $H = 100$ Oe with the sample being cooled in the absence (ZFC) and the presence (FC) of the magnetic field $H = 100$ Oe and (ii) magnetization as a function of the magnetic field measured at $T = 300$ K.