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Size and shape-controlled synthesis and characterization of $CoFe_2O_4$ nanoparticles embedded in a PVA-SiO_2 hybrid matrix

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ABSTRACT

This study presents the controlled synthesis and characterization of $CoFe_2O_4$ nanoparticles embedded in a PVA-SiO_2 hybrid matrix. The sol-gel method consists in the embedding of reactants (Co and Fe nitrates and 1,4-butanediol) in a matrix containing high molecular weight poly(vinylalcohol) and tetraethylorthosilicate, and in the formation and decomposition of succinate precursors followed by a controlled thermal decomposition (400–1000 °C). The thermal analysis and Fourier transformed infrared spectroscopy confirmed the formation of succinate precursors and hybrid matrix, while X-ray diffraction indicated the formation of single phase $CoFe_2O_4$. Transmission electron microscopy revealed the shape and size of $CoFe_2O_4$ nanoparticles, while scanning electron microscopy indicated the morphology of $CoFe_2O_4$/SiO_2-PVA particles. The particle size of ferrite is critically dependent on the annealing temperature and $CoFe_2O_4$:PVA-SiO_2 molar ratio.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) is a ferromagnetic oxide with high magnetic anisotropy, high saturation magnetization, high resistivity and good chemical and thermal stability [1]. $CoFe_2O_4$ crystallizes into an inverse spinel structure, where one half of the Fe^{3+} ions occupy the tetrahedral sites, while the other half are located in the octahedral sites together with Co^{2+} ions [2,3]. $CoFe_2O_4$ in powder or in dispersed fluid form, has received increasing attention due to its catalytic, electrical and magnetic properties that make it suitable for a wide range of applications (transformer cores, recording heads, antenna rods, loading coils, memory, microwave devices, catalysts, ferrofluids, magnetic refrigeration, magnetic sensors, drug delivery, gas detectors, sensors, solar energy conversion, stress and biomedical sensors, cellular therapy, tissue repair, etc.) [3–8].

As the synthesis method influences the $CoFe_2O_4$ morphological and structural features, various synthesis methods, such as sol-gel, co-precipitation, microemulsion, hydrothermal, combustion, sono-chemical, solid-state, complexation, microwave sintering, mechanical alloying, spray pyrolysis, reverse micelle, forced hydrolysis in polyol, pulsed laser deposition and ultrasonic cavitation have been reported [2,5,6,8–14]. Among them, combustion is a simple, low-cost, fast and high-yielding method leading to superior quality products, while co-precipitation and EDTA complexing routes enable crystallite size control [2,8]. Microwave sintering allows rapid volumetric heating, high production rates, low energy consumption and low sintering temperature [6]. Although the ceramic method is often used for industrial-scale production, it requires high energy consumption [12]. The sol-gel method is a simple and efficient route to produce materials with high purity, controlled crystallinity and homogenous particles size [4,5,7,10]. The nanoparticles are produced in-situ by decomposition of precursors, while the chelating gel is dried at relatively low temperatures [4].

To stabilize and reduce nanoparticle agglomeration, dispersion in a suitable matrix, such as resin, polymer or silica, can be used [15]. The addition of non-reactive species determines the growth of a solid oxide network around the nanoparticles, forming a doped gel with dispersed nanoparticles embedded in the network. The silica matrix provides a biocompatible, hydrophilic and non-toxic surface and may enhance the formation of single-phase spinel and the magnetic properties of nanocomposites [16,17]. Polyvinyl alcohol (PVA) is a semi-crystalline, non-toxic, biocompatible and biodegradable polymer with good chemical resistance, excellent film-forming capacity, as well as emulsifying and adhesive properties [11]. It prevents particle agglomeration and

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influences the particle size, magnetic properties and crystallinity of $CoFe_2O_4$ [5,10,11]. Hybrid matrices combine the advantages of both inorganic (thermal stability and rigidity, processability, chemical inertness, low cost, biocompatibility with sol-gel transitions) and organic (elasticity, ductility) components [18–20]. The thermal and mechanical properties of SiO_2 and the good flexibility of PVA make SiO_2-PVA hybrids important candidates for applications in the fields of catalysis, coatings, adsorption, pre-evaporation, medicine and enzyme immobilization [18–22]. SiO_2-PVA hybrids may embed materials in different forms such as monoliths, powders, tubes and fibers. The formation of the hybrid matrix consists in the embedding of PVA polymer in SiO_2, followed by a thermal decomposition of the organic part [23].

Numerous studies present the obtaining and properties of silica/PVA hybrids, $CoFe_2O_4$/PVA and $CoFe_2O_4/SiO_2$ nanocomposites [4,6,7,9–11,15–17,20–26]. However, there is scarce data on $CoFe_2O_4/SiO_2$-PVA nanocomposites. The iron(III) acetylacetonate/silica/PVA nanocomposites were synthetized and characterized by Ianasi et al. [23], while the formation of hybrid gels starting from tetraethyl orthosilicate (TEOS), PVA and 1,3-propanediol and the possibility of obtaining homogenously dispersed cobalt ferrite inside the silica matrix was studied by Stoia et al. [27].

In order to increase the crystallinity and size of nanoparticles, $CoFe_2O_4/SiO_2$-PVA nanocomposites were synthesized by a three-step sol-gel method. The used synthesis route was adapted after Stoia et al. [27]. The synthesis method consist in: (*i*) hybrid (SiO_2-PVA) matrix formation with embedding of reactants (Co and Fe nitrates, 1,4-butanediol (1,4-BD)), (*ii*) formation of succinate precursors and (*iii*) decomposition of succinate precursors with the formation of $CoFe_2O_4$ spinel. The advantage of this synthesis method is the decomposition of precursors at low temperatures, producing very reactive, low-crystalline oxide compounds that, by subsequent thermal treatments, leading to the formation of crystalline systems. The thermal behavior of $CoFe_2O_4/SiO_2$-PVA nanocomposites and the influence of the hybrid matrix and of the $CoFe_2O_4$/matrix ratio on the $CoFe_2O_4$ nanoparticles size and shape are also discussed and compared to that of PVA or silica matrix.

2. Materials and methods

Analytical grade reagents (Merck, Germany) were used without further purification. The average molecular weight of PVA was 145.000 g/mol. $CoFe_2O_4/SiO_2$-PVA nanocomposites were prepared by a sol-gel method. TEOS ($Si(OC_2H_5)_4$) dissolved in water was added drop-wise under stirring into the mixture of nitrates ($(Co(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$). Afterwards, 1,4-BD (OH—CH_2—CH_2—CH_2—CH_2—OH), 3% wt. PVA solution and ethanol (CH_3—CH_2—OH) were added drop-wise under continuous stirring, at 70 °C (Table 1). HNO_3 was added to adjust the acidity. The mixture was continuously stirred until complete dissolution and exposed to open air for slow gelation. The gels were dried at 40 °C (4 h), grounded in an agate mortar, preheated at 200 °C (4 h) and annealed at 400 °C (5 h), 600 °C (5 h), 800 °C (5 h) and 1000 °C (5 h).

The obtained nanocomposites were analyzed by thermal analysis (TG and DTA) using a SDT Q600 type instrument, in air up to 1000 °C at 10 °C min^{-1} rate and alumina standards. The Fourier transformed infrared (FT-IR) spectra were recorded on 1% KBr pellets using a Spectrum BX II spectrometer. X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD 6000 diffractometer, using Cr Kα radiation (λ = 2.29 Å) in order to remove fluorescence radiation of Fe, with a graphite monochromator, operated 40 kV and 30 mA, at room temperature. Transmission electron microscopy (TEM) observations carried out on a Hitachi HD2700 electron microscope were used to examine the size, shape and clustering of the nanoparticles, while the particle size distributions were determined using UTHSCSA ImageTool Software. The morphology and dispersion of samples were investigated by scanning electron microscopy (SEM) using a Hitachi SU8230 microscope.

3. Results and discussion

Fig. 1 shows the TG and DTA curves of gels dried at 40 °C and 200 °C. The DTA curve of SP10 gel at 40 °C displays four effects: (*i*) an endothermic effect (30–131 °C) with a maximum intensity at 93 °C (8% weight loss) attributed to residual water loss, (*ii*) an exothermic effect (131–169 °C) with a maximum at 153 °C (2% weight loss) corresponding to succinate precursors formation, (*iii*) an exothermic effect (169–348 °C) with a maximum at 289 °C (13% weight loss) corresponding to Co and Fe succinates decomposition to $CoFe_2O_4$, and (*iv*) an exothermic effect (349–534 °C) with a maximum at 388 °C (7% weight loss) attributed to PVA dehydration and to interactions of —C—OH (PVA) with Si—OH groups (SiO_2 matrix) resulting in the formation of C—O—Si bonds inside the SiO_2-PVA hybrid matrix. The formation of Co and Fe succinate precursors was observed up to 200 °C. This temperature was further considered in the thermal treatment as the formation temperature of succinate precursors. The DTA for SP10 gel, dried at 200 °C, presents an endothermic effect up to 199 °C corresponding to physically adsorbed water loss and an exothermic effect with a maximum at 400 °C (9% weight loss), attributed to C—O—Si bonds formation as a result of the interaction between C—OH (PVA) and Si—OH groups (SiO_2 matrix). The dispersion of PVA in SiO_2 increases the thermal stability of PVA [28].

Similar to SP10 gel, the thermal curves of SP30 gel dried at 40 °C display four effects: (*i*) an endothermic effect (30–101 °C) with a maximum intensity at 71 °C (4% weight loss), (*ii*) an exothermic effect (101–180 °C) with a maximum at 163 °C (11% weight loss), attributed to succinate precursors formation, (*iii*) an exothermic effect (180–306 °C) with a maximum at 274 °C (25% weight loss), corresponding to succinates decomposition and (*iv*) an exothermic effect (306–530 °C) with a maximum at 375 °C (29% weight loss), corresponding to PVA dehydration with the formation of C—O—Si bonds inside the hybrid matrix. The last effect is more pronounced in SP30 than in SP10 gel and appears also on the DTA curve of SP30 gel dried at

Table 1
Characteristics of synthesis route of the SP10-SP90 and P50 gels.

Sample	Quantity (mol)							
	$Co(NO_3)_2\ 6H_2O$	$Fe(NO_3)_3\ 9H_2O$	NO_3^-	1,4-BD	PVA	TEOS	Ethanol	H_2O
SP10	0.125	0.250	1	1	$3{\cdot}10^{-4}$	9.0	9.0	10
SP30	0.125	0.250	1	1	$3{\cdot}10^{-4}$	2.3	2.3	10
SP50	0.125	0.250	1	1	$3{\cdot}10^{-4}$	1.0	1.0	10
P50	0.125	0.250	1	1	$3{\cdot}10^{-4}$	–	–	10
SP70	0.125	0.250	1	1	$3{\cdot}10^{-4}$	0.43	0.43	10
SP90	0.125	0.250	1	1	$3{\cdot}10^{-4}$	0.11	0.11	10