Nanosized magnetic powders based on oxides

A A Nevmyvaka (A A Magaeva)¹, A G Pershina² and V I Itin¹

¹Tomsk Scientific Center SB RAS, 10/4, Akademichesky Ave., 634055, Tomsk, Russia
²Siberian State Medical University, 2 Moskowski Trakt, Tomsk, 634050, Russia

E-mail: kaa151@mail.ru

Abstract. The paper represents the method of obtaining and the main physical and chemical and magnetic characteristics of nanosized oxide-based powders. Nanoparticles are found to be nontoxic and can be used as carriers of drugs, sorption and desorption of nucleic acids, proteins and enzymes.

1. Introduction

In recent decade, magnetic nanosized powders have been studied in various fields of medicine and biology, since they have a lot of promising applications especially related to improving the quality of life of people [1-3]. The main advantages of magnetic nanoparticles are due to their sizes, developed specific surface, and low sedimentation rate in solutions, which determines high stability and a significant diffusion rate in the tissues of the body [4, 5]. An additional advantage is the single-domain nature of nanoparticles, which ensures the state of uniform magnetization in any external field and the superparamagnetic behavior caused by the weak interaction of very small domains. As a result, they do not retain magnetization after removal of the external magnetic field. For «in vivo» applications, magnetic nanoparticles should be from a non-toxic and non-immunogenic substance, have such a size to freely pass through the capillaries of the system and diffuse into tissues, as well as have a magnetization that gives a possiblility to control their behavior using the external magnetic field. For «in vitro» applications, the requirements to magnetic nanoparticles are much lower.

The above requirements are mainly determined by the method for the synthesis of nanoparticles, since the size and shape of particles, the presence of defects in the structure, the content of impurities, and magnetic properties depend on the chosen method.

This paper provides a review of the works performed at the Department for Structural Macrokinetics of Tomsk Scientific Center of SB RAS together with the scientists of the Siberian Medical University to obtain nanosized powders of various oxides by the method of mechanochemical synthesis (MCS) from salt systems and to study their phase composition, structural parameters and magnetic properties to use it for solving various problems of medicine.

2. Materials and methods

The stoichiometric and non-stoichiometric nanosized powders of oxide cubic ferrimagnetics (Fe₃O₄, CoₓFe₃₋ₓO₄, NiₓFe₃₋ₓO₄, MnₓFe₃₋ₓO₄, etc.) as well as the composite material SnO₂+Fe₃O₄ were obtained by the method mechanochemical synthesis from salt systems. Metal aqueous and non-aqueous chlorides, and carbonate and sodium hydroxide were used as starting materials for the synthesis...
reactions [6, 7]. To prevent the heating of the reaction mixture (rm) and the aggregation of nanoparticles, an inert component, sodium chloride, was added using the ratio \( m_{\text{rm}} : m_{\text{NaCl}} = 1:2 \) or 1:4. The initial mixtures were sealed in quenched steel drums with steel balls 5 mm in diameter. Mechnochemical synthesis was conducted in a planetary mill MPV (acceleration is 60 g). The activation time (\( \tau_{\text{MA}} \)) was varied and the ratio between the mass of balls and the mass of the powder was 20:1. The obtained product was calcinated in an oven at a temperature of 100°C for 60 m, washed in a centrifuge (ROTANTA 430 R) with distilled water to completely remove the salt matrix and dried at room temperature.

The phase composition, morphology, dispersity, and parameters of the structure of nanosized powders were analyzed using X-ray diffraction (Schimadzu XRD-6000 setup, CuK\(_\alpha\)) and transmission electron microscopy (EM-125 device); the specific surface area (S) was determined by the method of thermal desorption of nitrogen («SORBI N 4.1»); the chemical composition was determined using the X-ray fluorescence analysis («Schimadzu XRF-1800» setup). XRD data was processed using full-profile analysis (POWDER CELL 2.5 code) and the Scherrer equation. The average diameter was calculated from the values of the specific surface area and the particle density.

When studying the magnetic properties of synthesized oxides, the temperature dependences of the initial magnetic conductivity at a frequency of 10 kHz, as well as the magnetization curves and their derivatives obtained in pulsed magnetic fields with intensity of up to 3 T were analyzed using a technique described in [8].

3. Results and discussion

A study of the final products obtained by mechanochemical synthesis has shown that the powders of magnetic oxides consist of loosely bound nanosized spherical particles with a diameter of 3-15 nm, and the amount of particles with a size from 4 to 8 nm is approximately 65%. Figure 1 shows the particle size distribution for a cobalt ferrospinel nanopowder. The XRD microdiffractogram of the powders has a characteristic annular structure with a diffuse maximum in the region of small scattering angles belonging to the amorphous phase. All synthesized materials have a developed specific surface reaching 120-190 m\(^2\)/g, depending on the composition [7, 9].

![Figure 1. Histogram of the particle size distribution for nanoparticles CoFe\(_2\)O\(_4\).](image)

The lattice parameters, the coherent scattering (CSR) regions and the values of internal elastic microstresses \( \Delta d/d \) of the synthesized oxides were determined according to the XRD data. The nanosized powders obtained are oxides with a certain composition and in various cases may contain a small amount of hematite, an amorphous phase and iron monohydrate (\( \beta \)-FeO (OH) (the total amount of impurities does not exceed 12 vol.%)) (table 1) [6, 7, 10].

Significant changes in the fundamental magnetic properties of nanopowders obtained by the MCS method are due to mainly the size and the large contributions of surface anisotropy and the magnetoelastic component in comparison with massive samples. With a decrease in the size of the
structural element from $10^5$ to 3–15 nm, oxide ferrimagnetics exhibit characteristic features of a superparamagnetic state or a «cluster spin glass» state. The presence of a broad maximum of the values of $\mu(\mathcal{T})$ in the vicinity of $T=370$ K for the sample cooled in a magnetic field of 0.2 T (figure 2, curve 2) are the characteristic sign of realization of the magnetic state of the «spin glass» type. In this case, the saturation magnetization and the crystallographic anisotropy constant substantially decrease. The values of the specific saturation magnetization and the effective anisotropy field are given in table 2 [6].

**Table 1.** Specific surface, phase composition and structure parameters of nanosized ferrospinel powders.

| Sample     | Spinel, vol % | Hematite, vol % | Amorphous phase, vol % | Lattice parameter, nm | XRD (average grain size) | $\Delta d/d^*10^3$ | S, m$^2$/g |
|------------|---------------|-----------------|-----------------------|-----------------------|--------------------------|-------------------|------------|
| Fe$_3$O$_4$ | 90.3          | 5.7             | 4                     | 0.8382                | 11.0                     | 5.4               | 150        |
| MgFe$_2$O$_4$ | 88.5          | 5.5             | 6                     | 0.8397                | 11.2                     | 8.3               | 103        |
| LiFe$_5$O$_8$ | 88            | 6               | 6                     | 0.8336                | 9.8                      | 8.7               | 119        |
| MnFe$_2$O$_4$ | 90.6          | 4.4             | 5                     | 0.8542                | 11.2                     | 7.4               | 132        |
| CoFe$_2$O$_4$ | 90.8          | 3.2             | 6                     | 0.8376                | 9.2                      | 8.8               | 190        |
| CuFe$_2$O$_4$ | 95.8          | 4               | 0.2                   | 0.8375                | 9.5                      | 8.5               | 162        |

Since intense deformation impact (impact, friction) leads to the formation of «active» non-equilibrium states in nanoparticles during mechanochemical synthesis, the oxide nanopowders obtained by this method are characterized by nonstoichiometry, high elastic microstresses ($\Delta d/d$), the irregular degree of order in the arrangement of heterogeneous ions, the change in lattice parameters, and amorphization of the surface layer. Moreover, being in a metastable state, these materials tend to pass to a stable state during the aging process at room temperature. Evolution of the phase composition, structural parameters and magnetic properties indicates the development of a number of relaxation processes such as crystallization of the amorphous phase, dissolution of impurity phases in the spinel phase, etc. during the aging process [12].

![Figure 2](image_url)

**Figure 2.** Temperature dependences of the initial magnetic conductivity of the CoFe$_2$O$_4$ nanopowder. Sample is cooled in a zero magnetic field (1) and a field with 0.2 T (2).

Some synthesized nanopowders of oxide ferrimagnetics were studied for the purpose of their application in medicine and biology for pharmokinetic studies, as well as in separation and purification of biological substances. The «in vitro» studies of nanosized powders of magnetite and cobalt ferrospinels conducted in the laboratory testing the biological safety of medical products
(V.I. Shumakov Federal Research Center of Transplantology and Artificial Organs, Ministry of Health of the Russian Federation, No. POCC RU. 0001.21IM10, Moscow) have shown that these materials are tolerant and non-toxic. This result was confirmed by the studies conducted at the Research Institute of Fundamental and Clinical Immunology (Novosibirsk), where it was established that the magnetite nanoparticles had no toxic effect on the viability of macrophages in vitro and on the body.

**Table 2.** Magnetic properties of nanosized ferrospinel powders.

| Sample     | $\sigma^*$, G m$^3$/g | $H_A^{**}$, Oe |
|------------|------------------------|---------------|
| Fe$_3$O$_4$ | 26 (92)                | 520 (680)     |
| LiFe$_5$O$_8$ | 16 (65)              | 576 (640)     |
| MgFe$_2$O$_4$ | 6 (27)                | 550 (690)     |
| MnFe$_2$O$_4$ | 19 (80)               | 580 (640)     |
| CoFe$_2$O$_4$ | 22 (80)               | 2300 (12500)  |
| CuFe$_2$O$_4$ | 7.5 (25)              | 600 (1000)    |

Note: Parameters for bulk samples [11] are parenthesized.

$^*\sigma$ is the specific saturation magnetization.

$^{**}H$ is the effective strength of the anisotropy field.

Some obtained nanopowder oxides were investigated as universal carriers of biomolecules to create functional bionanocomposites which are stable in aqueous buffer solutions and controlled by an external magnetic field. Thus, a bionanocomposite with a high sorption activity relative to protein molecules (for example, bovine serum albumin and Taq polymerase enzyme) was created on the basis of CoFe$_2$O$_4$ and nonionic surfactant (Tween-20) [13], and a material for the sorption of DNA/RNA was developed on the basis of the composite material SnO$_2$+Fe$_3$O$_4$ [14]. The effective sorption index of these bionanocomposites exceeds the sorption index of widely used sorbents such as diatomite and silica by more than an order of magnitude.

The storage of enzymes on nanoparticles of cobalt ferrospinels substantially increases the duration of their enzymatic activity at room temperature. After storage for 40 days, the residual activity of enzyme not absorbed on nanoparticles is no more than 3% of the initial activity of enzyme, while the enzyme immobilized on nanoparticles retains more than 40% of the initial activity for 250 days (figure 3). The absence of a strong chemical bond between an enzyme and a nanoparticle and the magnetic properties of nanoparticles allow, if necessary, nanoparticles to be removed from a reaction mixture or enzymatic medication by the magnetic separation method [15].

![Figure 3: Dynamics of changes in the specific activity of Horseradish peroxidase during storage (37°C) in the presence of (2) and without (1) cobalt ferrite nanoparticles.](image-url)
Bionanoconjugate based on nanoparticles of cobalt ferrospinel with a high degree of selectivity was obtained to separate single-stranded specific nucleic acids from solution. Figure 4 shows that complementary oligonucleotides are efficiently bound from the solution and may be subsequently eluted from the nanoconjugate in water medium as a result of the temperature-induced melting of hydrogen bonds.

The bionanoconjugate obtained retains its superparamagnetic properties. It can be considered to be a magnetic particle modified with «sticky ends» and used to create biosensors. This invention can be used in the field of molecular genetic diagnostics [17].

4. Conclusion
The small size, the high specific surface, the ability to control the magnetic field, the tolerance and nontoxicity, as well as the high level of internal elastic microstresses, and the nonequilibrium and «active» state due to the method of obtaining are the advantages of nanopowders obtained by mechanochemical synthesis, which determines the possibility of further application in the field of medicine.

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