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ROZPRAWA DOKTORSKA

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Kształtowanie właściwości fizykochemicznych nanocząstek magnetytu za pomocą wybranych metod modyfikacji ich struktury, kształtu i powierzchni

w formie spójnego tematycznie cyklu artykułów opublikowanych w czasopismach naukowych

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Abstract

Fe_3O_4 nanoparticles have been extensively studied for many years due to their magnetic and electrical properties, surface area, and biocompatibility. Because the size, shape, and surface of nanoparticles define their properties, many methods have been developed to synthesize magnetite nanoparticles characterized by various shapes, from spherical, through cubic, to structures self-organizing under the influence of, for example, a magnetic field. The influence of the shape, size, and surface modification of Fe_3O_4 nanoparticles has been described in the specialist literature, especially in their use in medicine and catalysis. The literature includes information on the influence of oxidation, functionalization, and formation of core-shell structures on magnetic properties. In the case of describing the dielectric and electrical properties, these modifications have not been well studied and described so far (especially in a wide range of frequencies, temperatures, and, above all, in the nanoscale).

In connection with the above, a research thesis was formulated in this dissertation entitled “Modification of the physicochemical properties of magnetite nanoparticles using a selected method of changing their structure, shape and surface”, stating that physicochemical properties (catalytic activity, electrical conductivity, magnetic and dielectric properties) of ferrite nanoparticles depend not only on their chemical composition and size but also on the structure of the nanoparticles, their shape, functionalization, and surface oxidation. These changes can be controlled at the stage of nanoparticle synthesis and may define their future applications. In order to confirm the research thesis, research questions were formulated, the answers to which were presented in the thematically coherent series of articles published in international, peer-reviewed scientific journals. The presented cycle consists of selected papers published in journals with a total Impact Factor (IF) of 31.049 (the average IF per publication is 6.210) and a total number of MEiN points of 630. These publications present research on the structure, shape, oxidation, and functionalization of the magnetite surface and their influence on dielectric properties, electrical conductivity, magnetic properties, and catalytic activity.

The publication "Ultraslow electron-phonon scattering and polaron formation in magnetite" describes the effect of modifying the structure of magnetite nanoparticles by their isothermal annealing on electrical conductivity. Based on the obtained experimental data, a new model for describing the behavior of electrons in highly conductive magnetite was presented. According to it, in the low-frequency range, electrons behave in such a material as a virtual electron gas, while in the GHz frequency range, electrons-phonons scattering occurs. This interaction

generates polarons, which form large polarons responsible for high-frequency electrical conductivity in such material.

The influence of selective dissolution of the oxidized surface of magnetite and its functionalization by malonic acid on the electrical and catalytic properties of Fe_3O_4 is presented in the publication "Influence of magnetite nanoparticles surface dissolution, stabilization and functionalization by malonic acid on the catalytic activity, magnetic and electrical properties". It was shown that this method allows obtaining magnetite nanoparticles characterized by an increased value of electrical conductivity in comparison to unmodified nanoparticles. At the same time, it was shown that the tested nanoparticles, despite the smaller size of agglomerates, are characterized by much lower catalytic activity, which was associated with surface functionalization with malonic acid. An extension of the above research was presented in the publication "Influence of Magnetite Nanoparticles Shape and Spontaneous Surface Oxidation on the Electron Transport Mechanism", which describes the effect of organic modifiers on the growth and oxidation of the Fe_3O_4 surface. The results were correlated with dielectric and magnetic properties measurements, indicating possible applications of magnetite nanoparticles. It was confirmed, among others, that the use of triphenylphosphine allows the synthesis of magnetite nanoparticles with saturation magnetization of 55.2 emu/g and electrical conductivity 1000 times higher than in the case of synthesis without the use of an organic modifier.

Increased catalytic activity was observed and described for non-spherical shaped nanoparticles in the publication "Catalytic activity of non-spherical shaped magnetite nanoparticles in degradation of Sudan I, Rhodamine B and Methylene Blue dyes". The paper presented a synthesis method of non-spherical shaped magnetite nanoparticles and determined their catalytic activity in the degradation process of rhodamine B and methylene blue dyes. The possibility of nanomagnetite application in the processes of dye degradation in the high pH range was confirmed. Until now, these processes were usually carried out in an acidic environment due to the activation of the surface of magnetite nanoparticles at pH values below 4. Additionally, the publication proposed for the first time the mechanism of hydroxylation and degradation of Sudan I dye belonging to the group of azo dyes using the Fenton process and the light-assisted process UV. The non-linear changes observed in the UV-Vis spectra were linked to the formation of intermediate products and the occurrence of the hyperchromic effect.

The influence of the shape of magnetite nanoparticles on their magnetodielectric properties and absorption of microwave radiation is described in the publication "Microwave absorption by dextrin-magnetite nanocomposite in frequencies below 2.5 GHz: Role of magnetite content, shape and temperature on magneto-dielectric properties". Changes on the surface of magnetite nanoparticles during their slow growth into cubic forms significantly reduced the possibility of absorbing electromagnetic radiation. In the case of spherical nanoparticles, their surface is rich in structural defects, which results in increased losses in a wide frequency range. In addition, the reorientation of atoms on the surface of such nanoparticles also changes the ordering of spins on the surface of nanoparticles, reducing magnetic losses in cubic forms.

In conclusion, the research confirmed the thesis, indicating that ferrite nanoparticles' physicochemical properties (catalytic activity, magnetic and dielectric properties, and electrical conductivity) depend on their structure, shape, functionalization, and surface oxidation. The presented scientific publications indicate that an adequately modified method of synthesis, chemical, and thermal treatment allows controlling the properties of magnetite nanoparticles. It was also shown that at the synthesis stage, it is possible to modify the magnetodielectric properties and electrical conductivity by functionalizing their surface and synthesis nanoparticles of various shapes and degrees of oxidation. Moreover, it was shown that all changes in the shape, size, and surface of nanoparticles not only change their basic physicochemical properties (often in a drastic way) but also each of these modifications has a significant impact on future applications (as electromagnetic interference shielding materials, capacitors or catalysts).