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ZnO and ZrO_2 nanoparticles for applications in biology and medicine - growth and characterization

This thesis is devoted to the synthesis and characterization of oxide materials intended for potential applications in biology and medicine and is a complementary part of a research project co-implemented by two research groups from the Institute of Physics of the Polish Academy of Sciences and the Warsaw University of Life Sciences. One of the goals of the work is to develop new materials that could be used in the marking method (fluorescence labels), as an alternative for the traditionally used organic dyes. Materials intended for the supplementation of important microelements for a living organism are a separate topic of research. ZnO nanoparticles with iron content are presented in this range. One of the fundamental goals was to obtain materials with a submicron size, slightly larger than semiconductor quantum dots tested for biological applications. Their practical application was limited by difficulties related, inter alia, to toxicity and the lack of stability of the luminescence they emit, which is connected with the so-called 'fluorescence blinking'. The research work carried out so far has confirmed that the use of materials with sizes ranging from a few to several dozen nanometers prevents chaotic changes in luminescence and allows for the identification of the introduced objects by the biological system and their effective elimination. The work focuses on two matrices with a large gap: biodegradable zinc oxide and more stable zirconium dioxide, characterized by a high degree of biocompatibility. For the synthesis of the materials being the subject of the work, the microwave-assisted hydrothermal method was selected. It allows to control both the size, shape and optical properties of the obtained materials by modifying individual parameters of the technological process.

Much effort has gone into optimizing the technology for producing ZnO nanoparticles as the primary material for most biomedical applications. Despite the existence of extensive literature on the technology of ZnO nanoparticles production, it is still difficult to draw unambiguous conclusions that would link the influence of individual technological parameters with the properties of the obtained nanomaterials. The work focuses on the influence of the chemical composition of the initial reaction mixture on the basic properties of the obtained materials (shape, size, optical properties). The means for this task were measurements using scanning electron microscopy (*SEM*), X-ray diffraction (*X-rays*), photoluminescence (*PL*) and cathodoluminescence (*CL*). The conducted research showed the dependence of the morphology and optical properties of the obtained ZnO-based materials on the choice of zinc ion precursor salt (acetate, nitrate and zinc chloride), the precipitation reagent used (NaOH, KOH, NH_4OH) and the type of solvent (water, hydrogen peroxide, ethanol) in which the synthesis was carried out. The selection of appropriate precursors led to obtaining materials not only of different shapes and sizes, but also characterized by different values of the ratio of the intensity of the edge to the defect luminescence band (I_{NBE} / I_{DLE}). Its highest values were obtained for samples obtained from zinc chloride, while the lowest were typical for materials made of zinc nitrate. These samples became the basis for further, more detailed comparative studies. Among other things, the chemical composition analysis was carried out using following methods: *EDX* measurements (Energy dispersive X-Ray spectroscopy) were performed, Raman spectroscopy, Fourier transform infrared spectroscopy (*FTIR*) and thermogravimetric analysis (*TGA*) were used. Additionally, the dependence of luminescence spectra on the excitation power density was investigated using various methods of excitation of the tested materials (photoluminescence, radioluminescence, cathodoluminescence). Dynamic light scattering (*DLS*) measurements were performed to assess the stability of aqueous suspensions of nanopowders. The influence of additional heat treatment on materials made of zinc chloride characterized by the highest I_{NBE} / I_{DLE} ratio among all the obtained samples was also verified.

For most applications, such as labeling cancer cells or supplementing with micronutrients, doping is necessary. This thesis deals with this problem in the chapters on ZnO nanoparticles with europium ions (marker function) or iron ions (created for supplementation purposes). Based on the series of syntheses of ZnO:Eu nanoparticles that were carried out at various pressures ranging from 2 to 10 MPa it was found that this parameter affects the morphology of the obtained materials and their optical properties. The ZnO:Eu luminescence spectra obtained at 6 and 8 MPa revealed the presence of europium ions in strictly defined positions in the lattice, in the C_{3V} symmetry. The highest degree of chemical purity and the highest homogeneity were characteristic for nanoparticles obtained at 8 MPa. A separate chapter of the work concerned on ZnO: Fe nanoparticles created in order to supplement exogenous iron into a living organism. Surprising results were obtained by examining luminescence. Efficient luminescence quenching typical of bulky materials has not been observed, which opens the door to much considerations. The basic properties of the obtained materials were analyzed on the basis of luminescence, cathodoluminescence, *DC* and *AC* magnetic measurements.

Additional research topics included ZrO_2 nanoparticles. Based on the previous experience with this material it is characterized by greater stability in body fluids than ZnO and intended for longer observations. Various contents of Yb ions (concentration range from 0.5 to 20 mol %) were introduced into this matrix while maintaining the constant Pr concentration (0.5 mol%). As a result, ZrO_2 was partially or fully stabilized. The properties of the materials produced by the microwave assisted hydrothermal method were compared with the samples additionally annealed at 1200° C in the air atmosphere.

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