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ROZPRAWA DOKTORSKA

"Hybrydowe nanostruktury jednowymiarowe o podwyższonej aktywności fotokatalitycznej"

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Abstract

The aim of this work was to apply a hybrid method combining the sol-gel technique of preparing spinning solutions, the electrospinning process of polymer-precursor nanofibers and high-temperature calcination to produce ceramic ZnO nanofibers and ZnO:Yb³⁺, ZnO:Eu³⁺ and ZnO:Yb³⁺:Eu³⁺ and to investigate the influence of rare earth ion dopants on the structure, morphology, optical properties and photocatalytic activity of one-dimensional ZnO nanostructures. The first stage of the work included the preparation of homogeneous spinning solutions with the molar ratio of precursors in the range of 0.0075-0.0085 mol/dm³ and the concentration of PVP polymer equal to 10%. The solutions were spun in an electrostatic field with strictly defined process parameters, which resulted in obtaining defect-free polymerprecursor nanofibers with diameters in the range of 40-1000 nm. In the second stage, the electrospun 1D nanostructures were calcined at 500°C, which was determined based on TGA tests of polymer-precursor nanofibers. Based on the analysis of the morphology and structure of ceramic nanofibers obtained during the second stage, the polycrystalline nature of hybrid nanostructures was demonstrated with the morphology of individual nanoparticles sintered together to form the shape of a fiber with diameters in the range of 40-240 nm, characteristic for the electrospinning method. Based on the analysis of the results of the spectroscopic methods used in this work, the presence of the crystalline phase of ZnO in the form of wurtzite and the incorporation of Eu and Yb elements into the crystal lattice of zinc oxide in the form of tripositive ions were confirmed. In addition, based on X-ray diffraction patterns and the application of the Halder-Wagner method, it was possible to determine the size of crystallites that were reduced with the doping of the ZnO structure with europium and ytterbium ions, with a simultaneous increase in the deformation of the zinc oxide crystal lattice. Using a UV/Vis spectrophotometer, electromagnetic radiation absorption graphs were determined, which showed a shift of the absorption edge towards visible waves, and the Eg values determined from the Tauc formula showed a reduction from 3.02 eV for ZnO nanofibers to 2.55 eV for ZnO:Yb³⁺:Eu³⁺ nanostructures. The widening of absorption range of hybrid nanostructures influenced the increase in the photocatalytic activity of zinc oxide nanofibers simultaneously doped with Yb³⁺ and Eu³⁺ under visible light compared to ZnO nanostructures and the commercially used P25 photocatalyst.