FLUORESCENT PROPERTIES OF GD-DOPED ZNO NANONPOROUS NETWORKS & ITS APPLICATION IN OPTICAL BIOSENSING

Shulga A. 1, Butusov L.A. 1, 2, Boruleva E.A. 1, Chudinova G.K. 2, 3, Sheshko T.F. 1, Kurilkin V.V. 1, Kochneva M.V. 1

1 Peoples’ Friendship University of Russia (RUDN University), Miklukho-Maklaya str. 6, Moscow, Russia, 117198
2 Institute of General Physics. A. Prokhorov RAS, Vavilov str. 38, Moscow, Russia, 119991
3 National Research Nuclear University “MEPhI”, Kashirskoye sh., 31, Moscow, Russia, 115409

E-mail: aleksandra-box@mail.ru

Abstract. This research presents a study of the fluorescent properties of new materials based on gadolinium-doped zinc oxide nanoporous networks obtained by sol gel method on the surface of microcrystalline silicon. The effect of co-doping of different concentrations of Gd ions on the emission properties of ZnO nanoparticles has been investigated. Emissions of such biomolecules as protein, amino acids and porphyrin and its detection limits were studied for the purpose of practical application of Gd-doped ZnO nanonporous networks as an element of an optical biosensor technology.

1. Introduction

Recently, scientists have attracted special attention to nanoparticles, which have multifunctionality, especially nanoparticles that combine several properties, for example semiconducting, electro-optical and luminescent [1]. Such materials contribute to a significant expansion of their application and zinc oxide is one of them.

Zinc oxide is a thermally and chemically stable material, while it is biocompatible. On the basis these properties zinc oxide is in use at biological systems and biosensors.

The doped structures, such as [5-7] studied the effect of doping with cadmium, magnesium and sulfur on the structural characteristics of ZnO films by an x-ray diffraction method and observed an increase in the lattice parameter with increasing impurity concentration. There is also important research on doping semiconductors with gadolinium to increase or decrease photoluminescent properties of ZnO [8]. Areas of application of such materials are very diverse. Consequently, it is widely used in fabrication of various optoelectronic devices such as transparent conducting oxide, solar cells or flat panel displays. In some cases, for the selective determination of a biomolecule, it is necessary to reduce the intrinsic fluorescence of zinc oxide, which is possible due to the introduction of the dopant. Besides semiconducting properties, ZnO nanomaterials also exhibit various desirable traits for biosensing such as high catalytic efficiency, strong adsorption capability, and high isoelectric point (IEP; ~9.5) which are suitable for adsorption of certain proteins by electrostatic interaction.

Furthermore, high surface area, good stability, low toxicity, and high electron transfer capability also make them promising nanomaterials for biosensors [9].

Due to its unique optical, acoustic and electrical properties, zinc oxide has found application in gas sensors, varistors, and devices for generating surface acoustic waves. Being transparent in a wide spectral range, ZnO has a high resistance to irradiation, it is chemically etched and relatively cheap,
which makes it attractive for use in microelectronics [2,3]. Doping of ZnO films with some elements leads to an increase in the width of the forbidden band, an increase in the activation energy of the donor centers and their stability [4]. The authors [5-7] studied the effect of doping with cadmium, magnesium and sulfur on the structural characteristics of ZnO films by an x-ray diffraction method and observed an increase in the lattice parameter c with increasing impurity concentration. Doping elements of the III group - aluminum, gallium, and indium - allows to obtain n-ZnO films with high conductivity. Doping elements of the V group made it possible to obtain p-type conductivity. To successfully create light-emitting devices based on ZnO in the form of p-n junctions or optoelectronic devices on heterostructures using ZnO, careful studies of the properties of doped ZnO films are necessary. The most convenient is gadolinium because its excitation wavelength coincides with the substrate materials.

In this article we consider the behavior of nanosized ZnO doped Gd films with different weight ratios of dopant and zinc oxide, for example, interactions with biomolecule such as myoglobin (MB) of various concentrations.

2. Experiment
The preparation of materials based on zinc oxide is currently carried out using various techniques having both advantages and disadvantages. In the present work the sol-gel method was used, one of the most effective methods for the formation of films whose surface is structured at the nanolevel. (nanosize). Materials of ZnO-Gd (III), which have not been studied before, have been obtained. The change in their spectral characteristics has been studied with varying concentrations of dopant-gadolinium ion – 7.8,12 stoichiometrically percentage (wt%). These films are the basis of an optical biosensor device with fluorescent detection, designed to investigate biomacromolecules in concentrations of 10^-15M and even lower by fluorescence spectroscopy method.

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\text{Zn}^{2+}/\text{Gd}^{3+} + \text{C}_2\text{H}_5\text{OH} \rightarrow (=60^\circ\text{C} \rightarrow \text{sirring}) \rightarrow \text{ZnO/Gd}_2\text{O}_3 (\text{sol}) \rightarrow (\text{monoethanolamine}) \rightarrow \text{ZnO/Gd}_2\text{O}_3 (\text{sol/gel}) \rightarrow \text{depositing the seed layer of the sol onto a substrate} \rightarrow \text{dried in oven at 140}^\circ\text{C} \text{to obtain oxide films}
\]

Synthesis of undoped and Gd doped ZnO was carried out using analytical grade zinc acetate [(CH₃COO)₂Zn], gadolinium nitrate [Gd(NO₃)₃] and monoethanolamine (C₂H₂NO) in as-received condition. In the synthesis process, a required amount of zinc nitrate was completely dissolved in deionized water and a required amount of aqueous C₂H₂NO solution was added drop by drop to the aqueous zinc nitrate. The solution was stirred and maintained at room temperature for 40 min, and then kept at 60 °C for 2 h, until complete dissolution of the white precipitate. For maturing the solution was kept at ambient temperature (22 ± 2) °C for 2-7 days. After applying the seed layer sol thickness of 70 nm on a silicon substrates placed in a muffle furnace for drying at a temperature of 150 °C for 10 min, then annealed at a temperature of 500°C for 2 hours. The process of deposition and drying and annealing were repeated until the desired coating thickness. For the synthesis of Zn₁₋ₓGdxO (from 0.01 to 0.33) NPs, a calculated amount of gadolinium nitrate was mixed with zinc nitrate solution. The required amount of aqueous C₂H₂NO solution was added drop by drop to the homogenous mixture to get a white precipitate. Further, a similar procedure adopted for the preparation of undoped ZnO.

3. Results and discussion
In this research we obtained thin films of a hybrid material of zinc oxide doped with different percentage by mass (7,8,12 wt%). Gadolinium is making a significant contribution to its own fluorescence sensor. We investigated the possibilities of fluorescence analysis of thin films of myoglobin protein using these sensor variations. Figure 1A shows the emission spectra (λₑₓ=280nm) of myoglobin in concentrations from 10⁻⁴ to 10⁻¹² mg / ml on the ZnO sensor surface with 7% of dopant. We note that the bathochromic and hypsochromic shifts of the fluorescence maxima did not exceed 3-5 nm. We observe a fluorescence decreasing with decreasing protein concentration up 10⁻⁸
mg/ml of MB, then there is a linear dependence area and fluorescence ignition from $10^{-12}$ mg/ml of MB.

Figure 1B shows the fluorescence maximum values of all protein concentrations for three sensory surfaces doped with different amounts of phosphor. All three have a common feature - the ignition of fluorescence from $10^{-12}$ MB.

Fig. 1 A) fluorescence spectra of Myoglobin’s different concentrations ($10^{-4}$-$10^{-12}$ increment of dilution x100) on the surface of ZnO-Gd doped (7 wt%) ($\lambda_{ex}=280$nm) B) fluorescence response of the protein (MB) ($\lambda_{ex}=280$nm) at different concentrations on three different surfaces of ZnO (modified by 7, 8 and 12 weight percent of Gd)

In this case, the most significant are plates with 8 wt% of the Gd, which is almost 24 times higher than the base point without a protein, and 1.5 times exceeds 12 wt% of the Gd. The explanation of these phenomena is the task of our future research. Preliminary studies with a scanning electronic microscope using the example of 7% Gd are presented in Figure 2, these structures are nanoporous networks with a fairly large grain size of 8 μm, the average width of such filaments is 20-30 nm, while the length can reach several tens of μm.

Fig. 2 SEM images of ZnO modified by 7 weight percent of Gd

The excitation wavelength of 280nm corresponds to the excitation of a fragment of the molecule of myoglobin, the amino acid of tryptophan with emission in the region of 340-360nm, while we observe small "shoulders" in the region of 350-360nm associated with partial excitation of zinc oxide.
nanostructures (see electronic transition in this region). In addition to tryptophan, the protein contains
a porphyrin fragment, which, however, was not determined at concentrations below $10^{-6}$ mg / ml ($\lambda_{ex}=420$nm $\lambda_{em}=680$-710 nm).
The results obtained indicate good prospects for using gadolinium-doped zinc oxide structures as a
fluorescent optical sensor for detecting biomacromolecules in the near ultraviolet region, apparently a
quenching of the fluorescent response appears in the visible light region, which can also be used in
specific cases.

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5. References

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