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The effect of bovine myoglobin on ultraviolet fluorescence of gadolinium-doped zinc oxide films

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ZnO thin films doped with 0.1 mass% of Gd have been firstly developed with the aim of using as sensitive surfaces for bioanalysis with fluorescent registration. Gd-doped films were prepared by sol-gel and spin coating techniques on monocrystalline silicon supports. Adding Gd^{3+} ions resulted in a red shift maximum (λ_{em} = 380 nm) band of ZnO fluorescence by 8-10 nm. Bovine myoglobin (MB) at neutral pH =7 (isoelectric point) was deposited from solutions with concentrations of MB in the interval from 10^{-6} to 10^{-12} M on Gd-doped ZnO surfaces by spin coating techniques. This led to 5-8 % fluorescence quenching for 10^{-6} – 10^{-10} M MB concentrations and 20 % fluorescence enhancing for the 10^{-12} M one.

Keywords: ZnO thin film, gadolinium, sol-gel method, ultraviolet fluorescence, myoglobin (MB)

INTRODUCTION

In the last few decades, considerable attention has been paid to studies of zinc oxide thin films and composite thin film materials containing ZnO due to their photoluminescence properties. There is great interest in the ultraviolet luminescence (UVL) of ZnO, which band lays in the region of about 360 nm [1-5]. It was established that the intensity of UVL of ZnO-containing materials substantially depends on the type and the amount of various substances included in the film composition of ZnO, in particular, oxides of rare-earth elements [6-12]. Therefore, these substances with a narrow intense luminescence band can be used as the basis for the development of biosensor elements highly sensitive to bioobjects with a ratio «signal/noise» significantly more than one. The research on the development of composite materials, in which the intensity of the UVL would be enhanced in comparison with zinc oxide films, was carried out. The doping of zinc oxide film by metals, their oxides, and nonmetals was used to this purpose [13-15].

What is more, rare-earth ions have received considerable attention in terms of doping the films, because they have unique electronic configuration, and moreover, it becomes possible to significantly modify the optical properties of films.

In the present work, zinc oxide films doped with Gd^{3+} ions were obtained for the first time; the optical characteristics were studied by absorption and fluorescence spectroscopy. Optical properties of the films were tested on a model system containing different concentrations of bovine myoglobin solution.

EXPERIMENTAL

ZnO thin films doped by gadolinium (Gd) were synthesized using sol-gel method [16]. For the preparation of precursor sol, zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$ and gadolinium nitrate $Gd(NO_3)_2 \cdot 6H_2O$ were dissolved in ethanol (CH_3CH_2OH) at room temperature during an hour. Monoethanolamine ($HOCH_2CH_2NH_2$) was added as a stabilizer to the nitrate mixture. Glass substrates (15×15 mm) were thoroughly cleaned in ethanol, acetone and after that were boiled in a solution of distilled water, hydrogen peroxide (35 %) and NH_4OH (25%) in a volume ratio of 4:1:1 for 20 min. The prepared sol was deposited with a rotation speed of 3000 rpm in the centrifuge "Elekon" CLMN-P10-02 (Russia). Then, films were preheated to 130°C for 15 min to eliminate the organic residuals. Finally, the obtained films were annealed in air at 450°C for an hour in a muffle furnace.

Bovine myoglobin (Sigma-Aldrich) was used in concentrations of 10^{-8}, 10^{-10} and 10^{-12} M obtained from a base solution of 10^{-6} M (pH = 7.0) by sequential dilution. 20 µl of MB solution was applied on the surface of ZnO (Gd) films on a glass

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substrate by the spin coating method at a spin speed of 2000 rpm using a modified centrifuge "Elekon" CLMN-P10-02 (Russia). Fluorescence spectra of the samples were measured with a spectrofluorometer RF-5300pc (Shimadzu).

Fluorescence intensity was registered on 0.2 nm intervals, with slits of excitation and registration of 3 and 5 nm, respectively. Origin 8.1 software was used for data processing. Spectra processed by an "adjacent averaging" curve smoothing method (number of pixels for averaging was 20) were used for the calculation of maxima of fluorescent bands. The integral fluorescence was evaluated as an area beneath the curve of fluorescence intensity *vs* wavelength relationship in the 320-450 nm wavelength range. The use of integral intensity is convenient for unifying the results, including situations in which various devices with different optical characteristics were used.

RESULTS AND DISCUSSION

Figure 1 shows the fluorescence spectra at λ_{ex} = 280 nm for thin films of ZnO and ZnO doped with 0.1 mass% of Gd (280 nm myoglobin absorption maximum).

In the fluorescence spectra of ZnO films, there are two bands with maxima at 357 nm and 362 nm (Figure 1). Doping with Gd^{3+} leads to a decrease in the intensity of the shortwave band by 10% with a slight bathochromic shift (5 nm), as well as adduces to noticeable increase in the fluorescence intensity in the region of long wavelengths (λ_{em} = 389 nm) and the shift of the maximum fluorescence band with doping was 7 nm (λ_{em} = 382 nm).

Figure 2 A, B shows the fluorescence spectra at different concentrations of bovine myoglobin applied to the surface of zinc oxide and zinc oxide-Gd^{3+} films. There are differences in the interaction of bovine myoglobin with zinc oxide films and zinc oxide-Gd^{3+} films. In the case of (figure 2, A) zinc oxide films the maximal fluorescence intensity was observed at bovine myoglobin concentration of 10^{-6} M, while for the doped films at 10^{-10} M (λ_{em} = 358 nm). According to figure 2 the doping of films changes fluorescence intensity by 5% while without doping – by 10 nm.

Figure 3 A, B shows the change in the integral fluorescence (S) *versus* the concentration of bovine myoglobin on the surface of ZnO and ZnO films doped with 0.1 mass. % Gd, as an average of three parallel measurements. Obviously, doping with low concentrations of gadolinium qualitatively changes the fluorescent response of the system to different protein concentrations. Dependencies for ZnO undoped samples are not linear while for ZnO doped with Gd thin films they have a linear relationship.

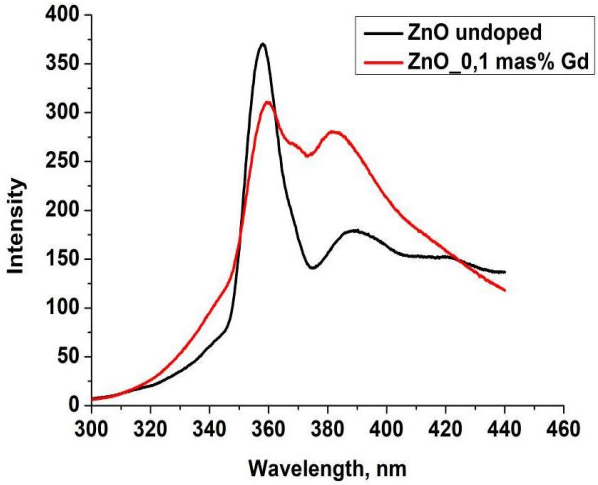

Figure 1. Fluorescence spectra of ZnO (black line) and ZnO-Gd^{3+} films (0.1 mass. % Gd) (red line)

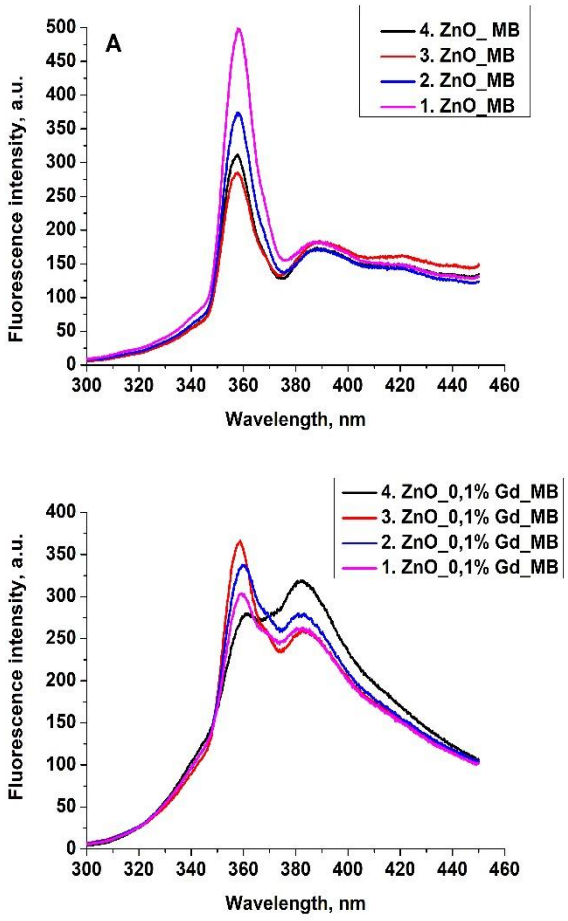

Figure 2. Fluorescence spectra of ZnO (A) and ZnO-Gd^{3+} (B) films (0.1 mass. % Gd) under the action of myoglobin. Myoglobin concentration in solution for depositing on films surfaces: **1** – 10^{-6}, **2** – 10^{-8}, **3** – 10^{-10}, **4** – 10^{-12} M.

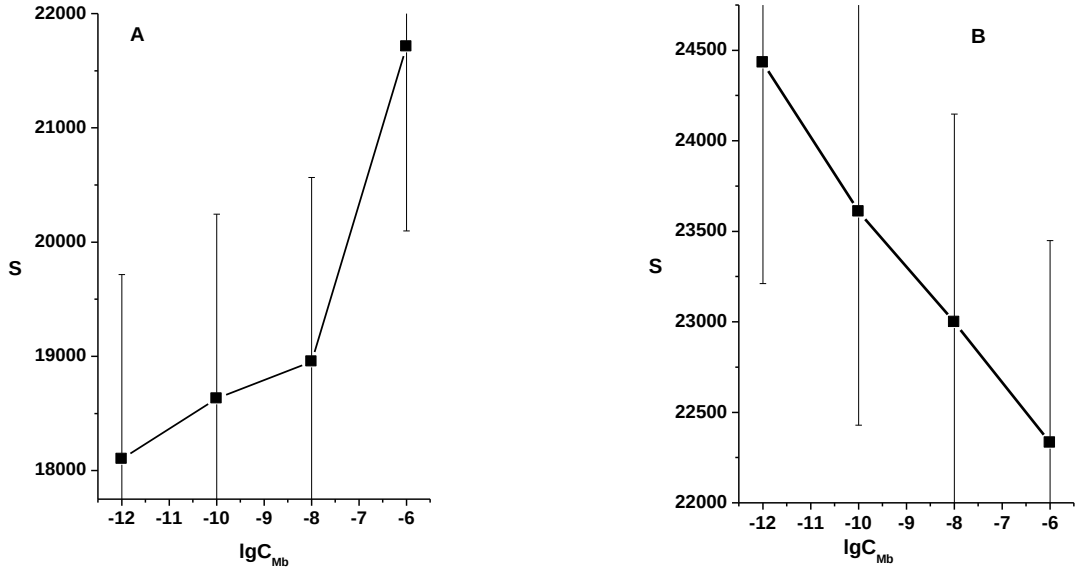

Figure 3. Dependence of the fluorescence intensity on the myoglobin concentration for ZnO (**A**) and ZnO-Gd^{3+} films (**B**).

Thus, on glass containing ZnO with dopant Gd^{3+}, small concentrations of protein can be determined.

CONCLUSIONS

Thin films of a new composite material were prepared by the sol-gel method. Zinc oxide doped with gadolinium was obtained, and its photoluminescence properties were studied in the UV range. The experiments revealed that the presence of Gd dopant significantly affects the change in the intensity of the photoluminescence of ZnO (λ_{em} = 340-400 nm) during the adsorption of globular protein (bovine myoglobin), and the luminescence intensity depends on the small protein concentration adsorbed on the films surface. Based on the above discussion the ZnO thin films doped with Gd^{3+} can be used as sensitive systems for fluorescent determination of very small quantities of protein.

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