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Luminescent properties of cerium (IV) -doped zinc oxide films

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Zinc oxide films doped by Ce^{4+} (0.1 – 1 molar %) were for the first time obtained by sol-gel technique and their spectral luminescent properties on monocrystalline silicon supports were studied with the aim to develop sensitive surfaces for biosensor devices. It was found that adding Ce^{4+} enhances the ultraviolet luminescence (UVL) of ZnO films by a factor of 7 (0.7 % mass Ce^{4+}). Films structures were controlled by SEM. Changes in UVL (λex = 280 nm, λem = 356 nm) of ZnO and ZnO-Ce^{4+} films were investigated under the action of bovine myoglobin (10^{-8} – 10^{-12} M, deposited on the film surface by a spin-coating method).

Keywords: sol-gel method, zinc oxide, cerium, optical biosensors, new materials, photoluminescence

INTRODUCTION

In recent years the need for sensitive, high-speed and also economic thin-film materials for various branches of science and equipment grows. In this regard most prospective are thin films of cerium dioxide which are successfully used in the developing fields of lighting industry and electronic equipments. Cerium dioxide and materials on its basis possess a wide range of applications in the industry, including production of biomedications, fuel elements [1], three-route catalysts [2], sensors [3], and production of fire-resistant materials. It is interesting to researchers of CeO_2 as an inorganic antioxidant which effectively protects live systems from oxidizing stress [4].

Cerium dioxide is a wide-gap semiconductor material with a band gap of ~ 3.2 eV (which is comparable to the band gap of zinc oxide — 3.4 eV). CeO_2 is optically transparent in the visible region of the spectrum. Its absorption band is located in the UV region of the spectrum at wavelengths of about 320 nm [5].

Cerium has good luminescent properties and application prospects for chemical sensors, as a dopant in matrices of other materials [6–9]. As an impurity, Ce attracts attention due to its special optical and catalytic properties, resulting from the presence of shielded 4f levels, and the redox pair Ce^{3+}/Ce^{4+} [10]. Cerium oxides are characterized by high catalytic activity. The reason for this is the instability of oxygen stoichiometry, which causes a fairly free $Ce^{3+} \rightarrow Ce^{4+}$ transition and a reverse transition [10]. Thus, cerium oxide is always mixed and contains CeO_2 and Ce_2O_3 in various ratios. Also due to this feature, cerium oxide has a high ionic conductivity of oxygen, and therefore it is of interest as a material for solid-state oxide fuel cells in an impurity form.

Among the numerous functional oxide nanomaterials, ZnO oxide doped with CeO_2, which is of particular interest due to a set of specific properties, was chosen as the object of study in this work: high chemical and thermal stability, and numerous practical applications, including the use of highly efficient catalysts, sorbents, sensors, solid electrolytes.

On the basis of all the above, the purpose of this work was to create a new composite material based on zinc oxide doped with different amounts of cerium oxide and to study the optical properties of the samples: change in the fluorescence of the material obtained. Influence of myoglobin (MB) in various concentrations on ZnO and ZnO-Ce^{4+} UVL was studied.

EXPERIMENTAL

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 nano level (nanosize). The change in their spectral characteristics was studied with varying concentrations of dopant-cerium ion – 0.1-1 stoichiometric percentage (mass %). These films are the basis of an optical biosensor device with

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fluorescent detection, designed to investigate biomacromolecules in low concentrations by fluorescence spectroscopy method.

Sample preparation was carried out in the following order:

$Zn^{2+}/Ce^{4+} + C_2H_5OH \rightarrow (\approx 60\ °C \rightarrow$ stirring) $\rightarrow ZnO/CeO_4$ (sol) $\rightarrow$ (monoethanolamine) $\rightarrow ZnO/CeO_4$ (sol/gel) $\rightarrow$ depositing the seed layer of the sol onto a substrate $\rightarrow$ drying in an oven at 140 °C to obtain oxide films.

Synthesis of undoped and Ce-doped ZnO was carried out using analytical grade zinc acetate [$(CH_3COO)_2Zn$], cerium acetate [$Ce(CH_3COO)_3$] and monoethanolamine (C_2H_2NO) in as-received condition. In the synthesis process, a required amount of zinc acetate was completely dissolved in deionized water and a required amount of aqueous C_2H_2NO solution was added dropwise to the aqueous zinc acetate. 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 with thickness of 70 nm on a silicon substrate 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 h. The processes of deposition, drying and annealing were repeated until the desired coating thickness. For the synthesis of $Zn_{1-x}CeO_x$ (from 0.01 to 0.33) NPs, a calculated amount of cerium acetate was mixed with zinc acetate solution. The required amount of aqueous C_2H_2NO solution was added dropwise to the homogenous mixture to get a white precipitate. Further, a similar procedure was adopted for the preparation of undoped ZnO.

Bovine myoglobin (Sigma-Aldrich Co) (Mb) solutions were prepared in distilled water. 20 µl of Mb solution was applied on the surface of ZnO-Ce^{4+} films on a monocrystalline silicon substrate by a spin-coating method (2000 rpm) on a centrifuge "Elekon" CLMN-P10-02 (Russia). Fluorescence spectra of the samples were measured with a spectrofluorometer RF-5300pc (Shimadzu).

RESULTS AND DISCUSSION

ZnO films with a fluorescence intensity of 40 relative units were obtained. Doping with cerium leads to an increase in luminescence by a factor of 7 with a maximum gain in films containing 0.7 % cerium. Films containing 0.7 wt. % cerium were further used to study changes in UV light by the action of bovine myoglobin. The adsorption of Mb was found to reduce the intensity of UV light (Figure 1). The dependence of the intensity of UV light (λ_{em} = 280 nm) on the concentration of Mb is nonlinear, the intensity decreases several times as compared with undoped zinc oxide.

The excitation wavelength of 280 nm corresponds to tryptophan in the myoglobin globule with emission in the region of 340-360 nm, while we observe small “shoulders” in the region of 350-360 nm. In addition to tryptophan, the protein contains a porphyrin prosthetic group, which, however, was not detected at concentrations below 10^{-6} mg/ml (λ_{ex}) = 420 nm.

The band at 356 nm belongs to ZnO, which is evident from Figure 1 showing the spectrum of ZnO without myoglobin. The shape of the spectrum does not change when myoglobin is applied. Hence, MB influence on ZnO UVL is negligible. The longwave fluorescence of ZnO and ZnO-Ce^{4+} is determined by the defects of the ZnO crystal lattice, so the fluorescence at 630 nm (Figure 2) is due to interstitial oxygen atoms in the ZnO lattice [11] Changes in the concentration of myoglobin have little effect on the long-wave fluorescence of the films.

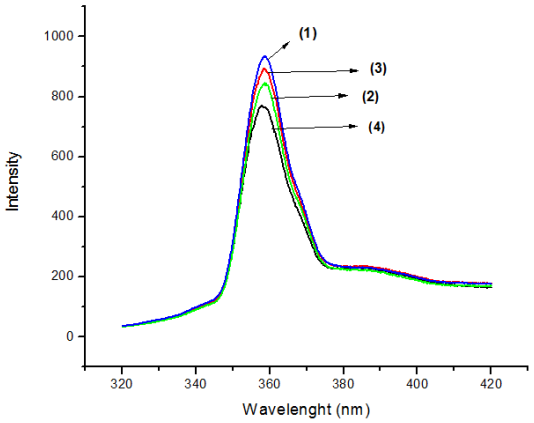

Figure 1. Fluorescence spectra at λ_{ex} = 280 nm of ZnO-Ce^{4+} film without Mb (1) and ZnO-Ce^{4+} film with Mb 10^{-8} M (2), 10^{-10} M (3), 10^{-12} M (4).

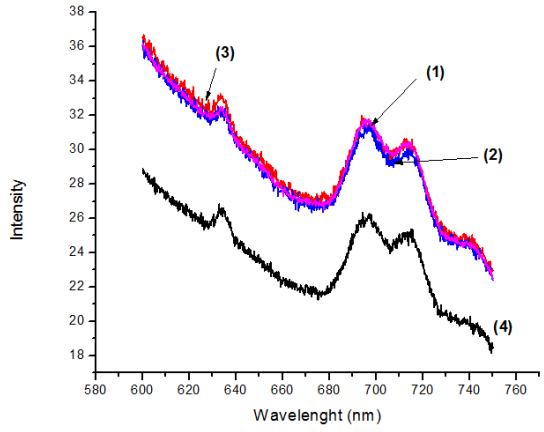

Figure 2. Fluorescence spectra at λ_{ex} = 420 nm of ZnO-Ce^{4+} film without Mb (1) and ZnO-Ce^{4+} film with Mb 10^{-8} M (2), 10^{-10} M (3), 10^{-12} M (4).

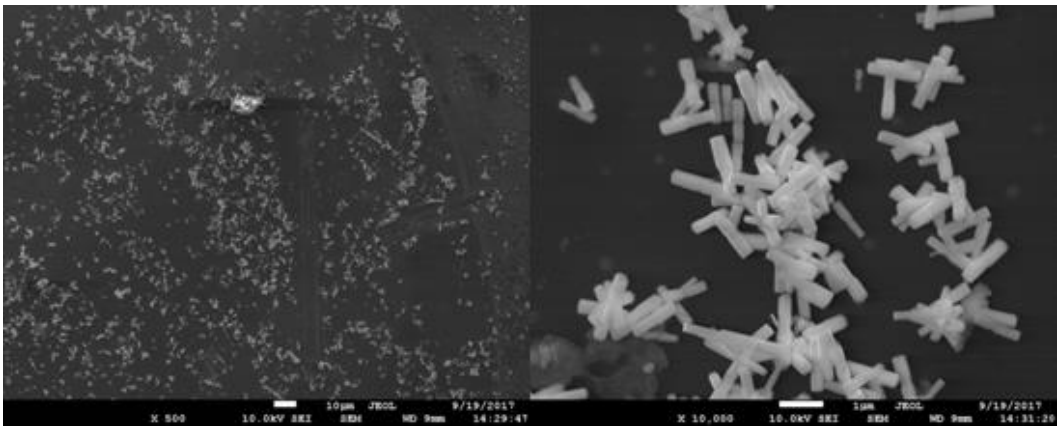

Figure 3. SEM images of ZnO.

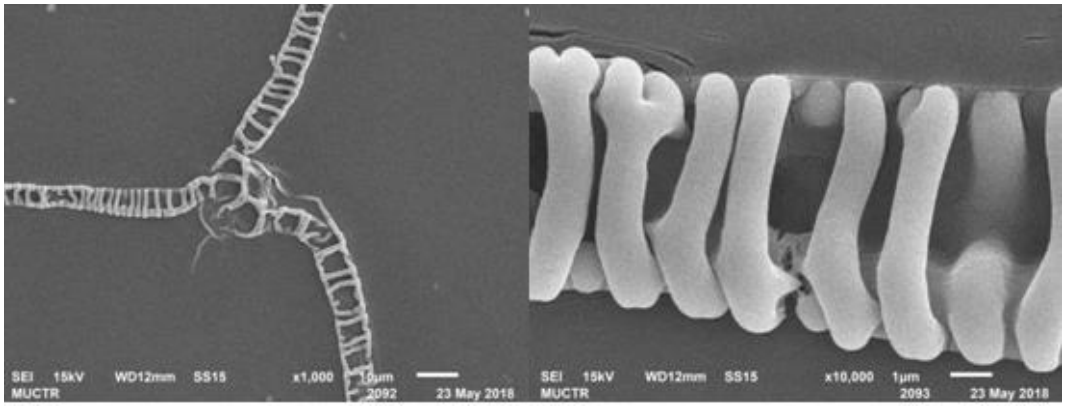

Figure 4. SEM images of ZnO modified by 0.7 weight percent of Ce.

The results indicate a good perspective of cerium-doped zinc oxide structures as a fluorescent optical sensor for detecting biomacromolecules in the near ultraviolet region, apparently in the visible light region, quenching of the fluorescent response appears, which can also be used in specific cases.
the scanning electron microscope image of ZnO and ZnO-Ce^{4+} shows a significant change in the surface relief (figures 3 and 4). in the first case, the structures are cylinders with a size of about 10 μm. in figure 4, the structures are "bones" with a size of 8 μm, the average width of such threads is 20-30 μm, and the length can reach several tens of μm. thus in doped materials the size and shape of the structures of zno cylinders changes and their ordered aggregation occurs.

CONCLUSIONS

Studies of films of zinc oxide doped with cerium using a sol-gel method were carried out. Ce^{4+}-doping of ZnO films leads to UVL enhancing by a factor of 7. Bovine myoglobin adsorption on ZnO-Ce^{4+} films surfaces causes UVL quenching by 0.7 % at concentrations of 10^{-8}, 10^{-10} and 10^{-12} M, correspondingly. Noticeable changes in the intensity of UV light of the material obtained by us show its promise as a recording element of a biosensor device with fluorescence detection for the qualitative and quantitative determination of protein with high sensitivity.

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