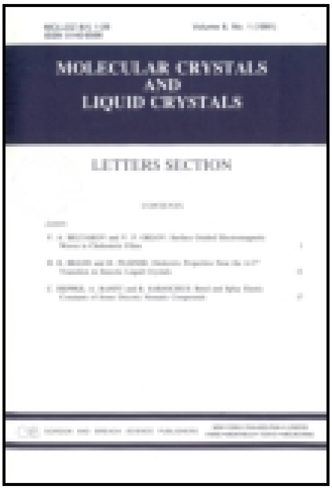

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Nanophotonic, Electro- and Magnetoactive Nanocomposites for Printing and Packaging

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The possibility of usage of printed films with nanosized ZnO particles for detection of freshness/spoilage of packaged products was analyzed. The influence of model amines which emerge in meat and fish during storage on intensity of photoluminescence of nano-ZnO films was investigated. The luminescence is quenched more intensively with the increase of concentration of the amines, which enables determination of the stage of spoilage of packaged food. The processes that occur in ZnO nanoparticles contacting with amines were explained on absorption spectra.

Keywords Nanophotonics; nanocomposites; ZnO; smart packaging; printing

1. Introduction

Application of photo-, electro- and magnetoactive composites in organic polymer layers and areas with nanophotonic, electromagnetic as well as photocatalytic properties by printing methods onto packaging materials as elements of "smart" packaging is very promising [1]. Such systems can track and alert to the processes that occur in packaged food during its storage by changing the intensity of luminescence while being exposed to light or the electric potential or change their magnetic properties in case of usage of magnetic-luminescent nanocomposites, therefore serving as "intelligent" systems for packaging.

The concept of smart packaging includes "intelligent" packaging, which contains some internal or external indicator for providing information about the state of a packaged product. Such packaging systems are aimed at monitoring the quality of a product and the state of environment inside or outside a package during storage therefore predicting or measuring a safe period of shelf life, informing a customer about the safety of consuming a product etc [2,3,4,5]. This ability of "intelligent" packaging to "communicate" with a customer is based on optical, mechanical, electronic and other properties of functional elements of packaging materials. These elements, indicators or sensors, can consist of ink compositions, applied to the surface of packaging materials by different techniques, including printing.

Detecting the process of spoilage of packaged products and alerting a customer to the results can enhance the safety of food consumption and prevent food poisoning. "Intelligent" system for packaging for spoilage indication can be based on changes in intensity of luminescence while being exposed to light or the electric potential or changes in magnetic properties in case of usage of magnetic-luminescent nanocomposites.

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Among the materials for smart spoilage indicators and sensors nanosized ZnO is considered to be quite promising due to the following reasons. ZnO nanoparticles possess a high surface-to-volume ratio and take part in specific interactions with organic functional groups [6]. Besides, nano-ZnO can serve as UV light and ionizing radiation barrier and a biosensor to identify proteins [7]. Nanosized ZnO is also used in antimicrobial nanocomposite films for food packaging [8]. Moreover, ZnO being a safe food additive enables the usage of it for food packaging [9].

The aim of the investigation is to study nano-ZnO films as model systems for nanophotonic devices and printed sensors, which can serve as spoilage indicators due to luminescence intensity changes in the presence of compounds that emerge in food products during storage.

2. Materials for Nanocomposites and Methods of Deposition onto Surfaces

Amines. Compounds emerge in food as a result of spoilade usually because of an oxidative process effected by bacteria, yeasts, and fungi, which transform food carbohydrates, proteins, and fats to low-molecular-weight molecules, including carbon dioxide (CO_2), lactic and acetic acids, aldehydes, alcohols (ethanol), hydrogen sulphide, nitrogen-containing molecules (ammonia), and amines related to the original amino acids that make up the protein [10]. Amines such as dopamine, tyramine, tryptamine, ahmatyn, and histamine were used as model substances which emerge in protein products during storage. These are volatile amines, responsible for the smell of rotting protein of meat, poultry etc.

ZnO for detection of amines. There are mentions of employing ZnO nanoparticles as a component of smart packaging for detecting amines which emerge in packaged products during storage. Undoped ZnO, Al_2O_3-doped, and SnO_2-doped ZnO thin films exhibit sensitivity to low concentrations of dimethylamine and trimethylamine, which emerge is fish and other seafood as a result of spoilage [11,12]. Nanocomposite of SnO_2 nanoparticles doped with 5–15 wt% ZnO microrods was claimed to detect trimethylamine too [13]. Fluorescent film based on ZnO nanoparticles is sensitive to the presence of amine gas, which makes possible to develop this film into amine sensor device [14]. Undoped and fluorine-doped nanostructured ZnO thin films are able to change photoluminescence depending on concentration of volatile organic compounds such as ethanol and trimethyl amine [15]. Therefore, there are mentions of ZnO serving as spoilage indicator, however, futher investigation is needed to correlate changes of properties of ZnO films with the changes in composition of packaged food with ageing.

ZnO nanocomposites. Stabilization of ZnO nanoparticles in solutions is crusial for further deposition onto the surfaces. It is often achieved by incorporation of nanoparticles into matrixes, such as clay matrixes [16], epoxy matrixes [17]. Nanoparticles prepared by means of organic-ligand-assisted hydrothermal conditions with various organic modifiers (e.g. hexanol) can change their surface from hydrophilic to hydrophobic, which can significantly enhance the dispersion of these particles in polymer matrixes [18]. Amines such as poly(vinyl formamide) and poly(vinyl amine) have great potential as adhesion promoters in the formation of stable metal/polymer joints [19]. Alkenes, amines, and alcohols are mentioned to form covalent bonds with the ZnO surface, thereby facilitating adhesion to the polymer [20]. ZnO was mentioned to be dispersed in the chitosan solution to form a ZnO/chitosan composite matrix [21]. It is possible to use oil varnish and polyvinyl acetate dispersion for stabilization of ZnO nanoparticles for futher application to the surfaces by printing techniques.

Nanocomposites containing nanoscale Fe_3O_4 as a magnetic component and nano-ZnO as a fluorescent component, besides freshness/spoilage indication, can also perform antimicrobial functions in packaging to extend the shelf life of food products, serving as "active" systems for packaging. Nanocomposites with CdS, CdSe, and similar ones may be accounted as the components for materials with electroluminescent properties for applications in active informational packaging. It is mentioned that luminescent nanocrystals such as CdSe, CdTe, and ZnSe show great promise in molecular detection of aldehydes [22]. There are mentions of well-aligned arrays of CdS-ZnO composite nanorods grown on indium tin oxide substrates [23].

3. Experimental Procedures

Colloidal ZnO nanocrystals were obtained from zinc acetate $ZnAc_2$ ($Zn(CH_3COO)_2$), sodium hydroxide (NaOH), and dry doubly-distiled ethanol (C_2H_5OH) [24]. ZnO nanocrystals in colloidal solution were stabilized with oil varnish and polyvinyl acetate dispersion. Nano-ZnO films were deposited onto polymer surfaces by ink-jet and screen printing. Magnetic fluid was obtained employing the method invented by E. E. Bibik [25]. Luminescent-magnetic nanocomposite material was synthesized from colloidal suspension of ZnO and magnetic fluid (nanosized Fe_3O_4). Polystyrene was used as a polymer matrix.

The luminescent spectra were recorded with a fluorescence spectrometer (Perkin Elmer, LS 55). The absorption spectra (optical density) were recorded with a spectrophotometer (Analytik Jena, Specord 210).

4. Results and Discussion

The influence of bioamines on ZnO films was investigated by analyzing the luminescence and absorption spectra of the films.

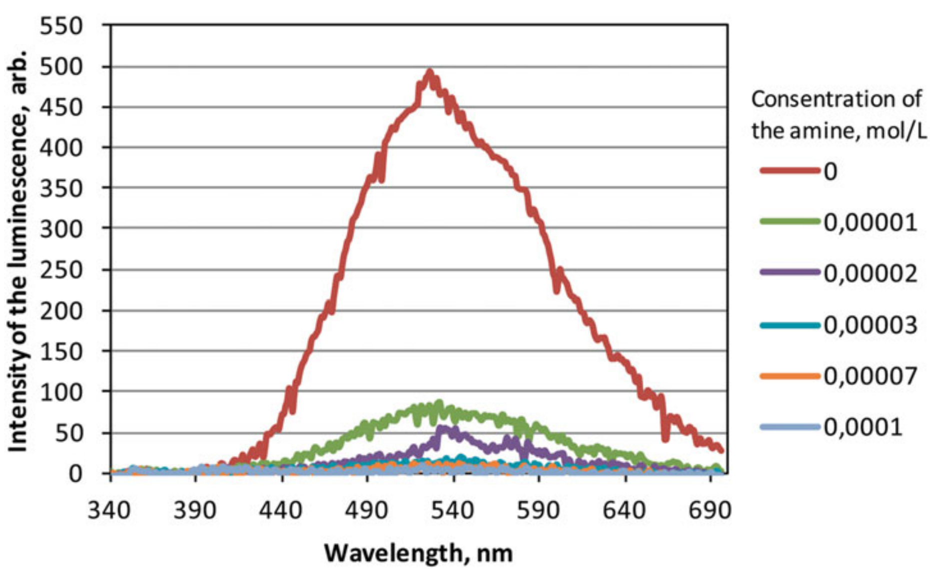

Figure 1. Luminescence spectra of ZnO in the presence of dopamine. $[ZnO] = 2 \cdot 10^{-3}$ mol/L, $\lambda_{irr} =$ 340 nm.

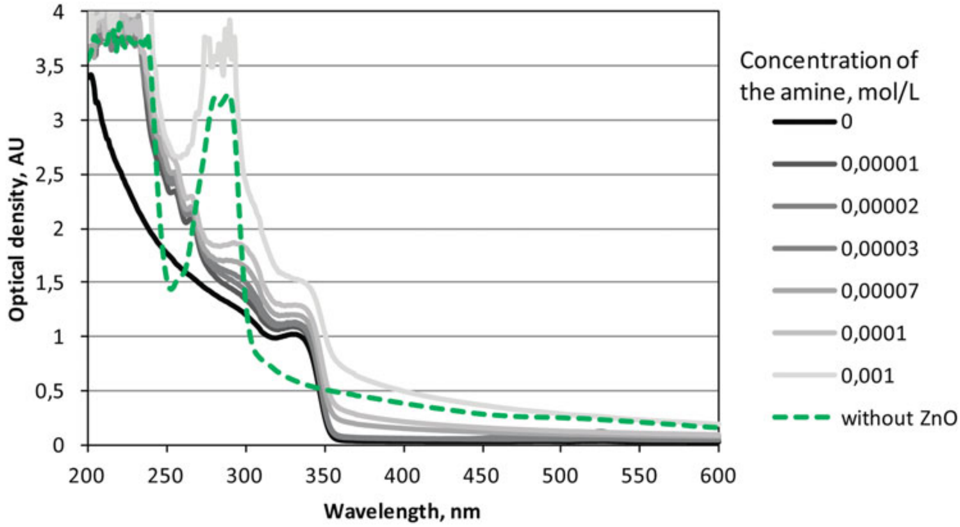

Figure 2. Absorption spectra of ZnO in the presence of dopamine. [ZnO] = $2{\cdot}10^{-3}$ mol/L.

The influence of dopamine on the intensity of luminescence of nano-ZnO films is demonstrated in Fig. 1.

As can be seen from Fig. 1, the quenching of the luminescence of nano-ZnO film by dopamine is significant. This fact can be confirmed and explained by the analysis of the absorption spectra of dopamine with nano-ZnO (Fig. 2). With the increase of the concentration of dopamine in the system, it absorbs light in UV region of the spectrum

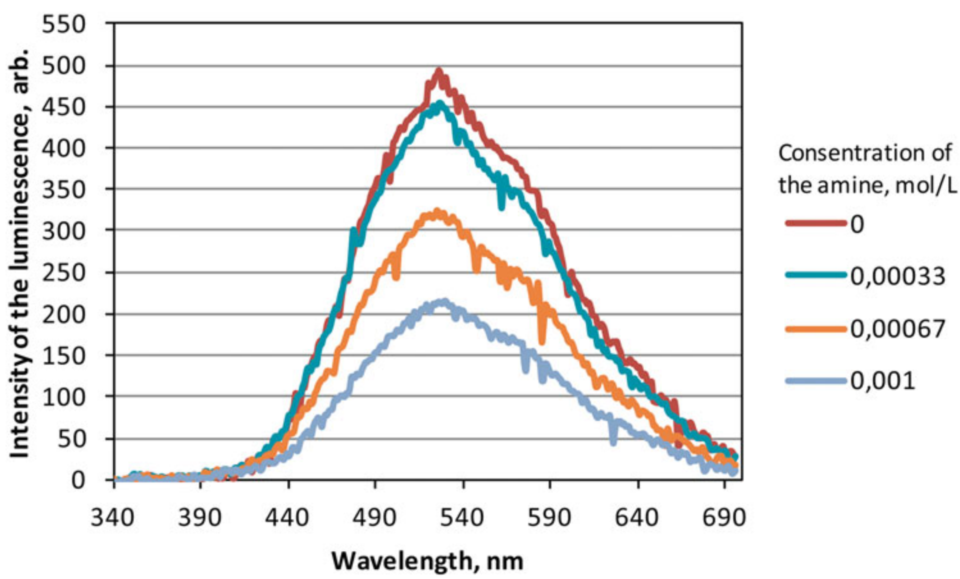

Figure 3. Luminescence spectra of ZnO in the presence of tyramine. [ZnO] = $2{\cdot}10^{-3}$ mol/L, λ_{irr} = 340 nm.

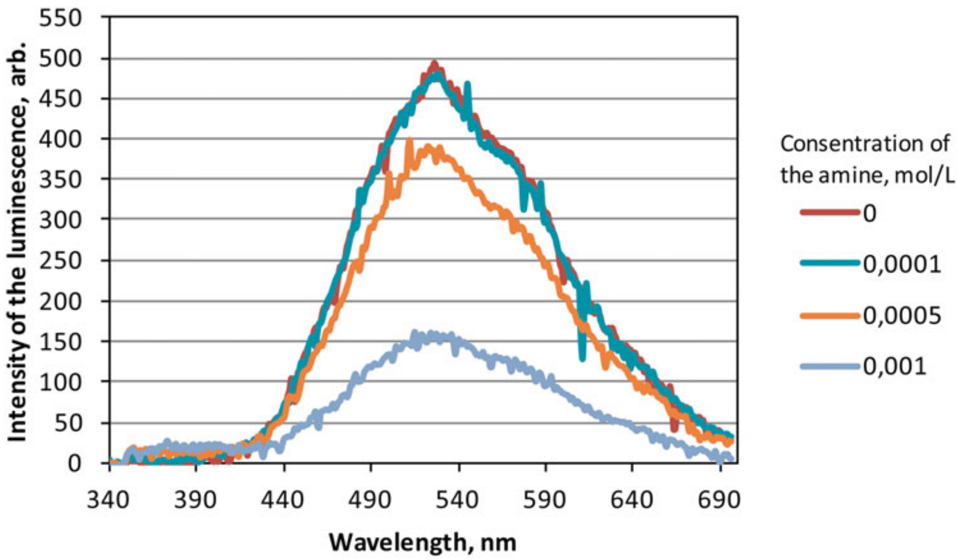

Figure 4. Luminescence spectra of ZnO in the presence of tryptamine. [ZnO] = $2{\cdot}10^{-3}$ mol/L, λ_{irr} = 340 nm.

much more significantly, therefore blocking light from excitation of the luminescence of nano-ZnO.

In case of tyramine (Fig. 3), tryptamine (Fig. 4), and histamine (Fig. 5) the behavior of luminescence spectra is similar to dopamine, except the quenching of the luminescence is less intensive, yet still significant.

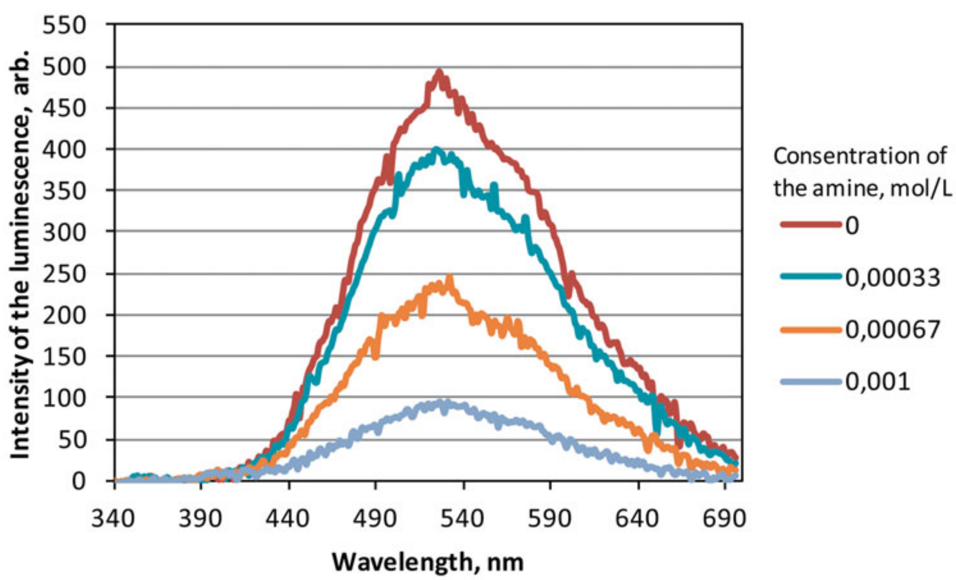

Figure 5. Luminescence spectra of ZnO in the presence of histamine. [ZnO] = $2{\cdot}10^{-3}$ mol/L, λ_{irr} = 340 nm.

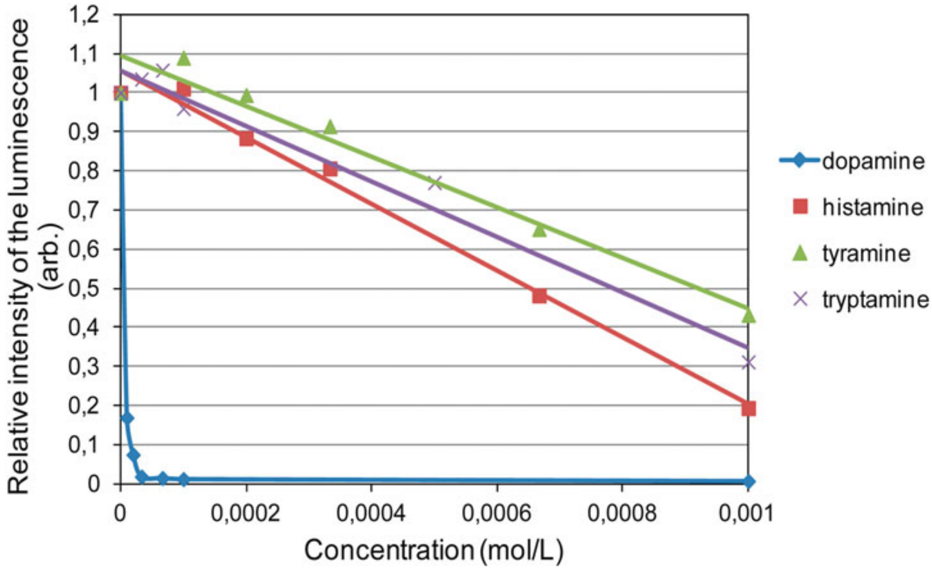

Figure 6. The change of the luminescence intensity of nano-ZnO films depending on concentration of the amines. [ZnO] = $2{\cdot}10^{-3}$ mol/L, λ_{irr} = 340 nm.

Quite different situation can be observed from experimental data with luminescence spectra of histamine with nano-ZnO. Figure 5 shows that at the concentration of histamine 10^{-4} mol/L a slight decrease in the intensity of the luminescence was registered, while at the concentration of histamine 10^{-3} mol/L the quenching of the luminescence was significant.

The change of the maximum luminescence intensity of nano-ZnO films in the presence of dopamine, tyramine, tryptamine, and histamine is depicted in Fig. 6 for peaks of luminescence spectra at 540 nm. As can be seen from Fig. 6, the intensity of the luminescence

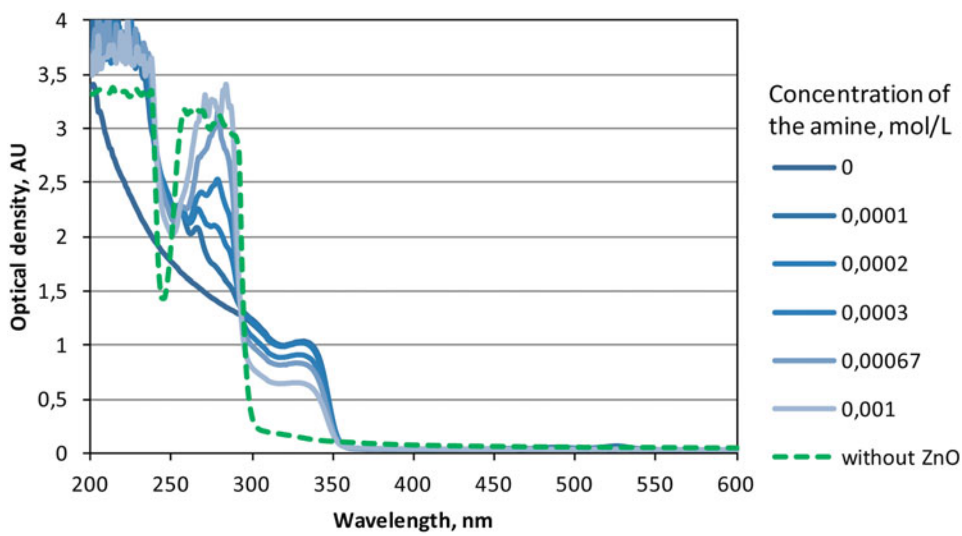

Figure 7. Absorption spectra of ZnO in the presence of tyramine. [ZnO] = $2{\cdot}10^{-3}$ mol/L.

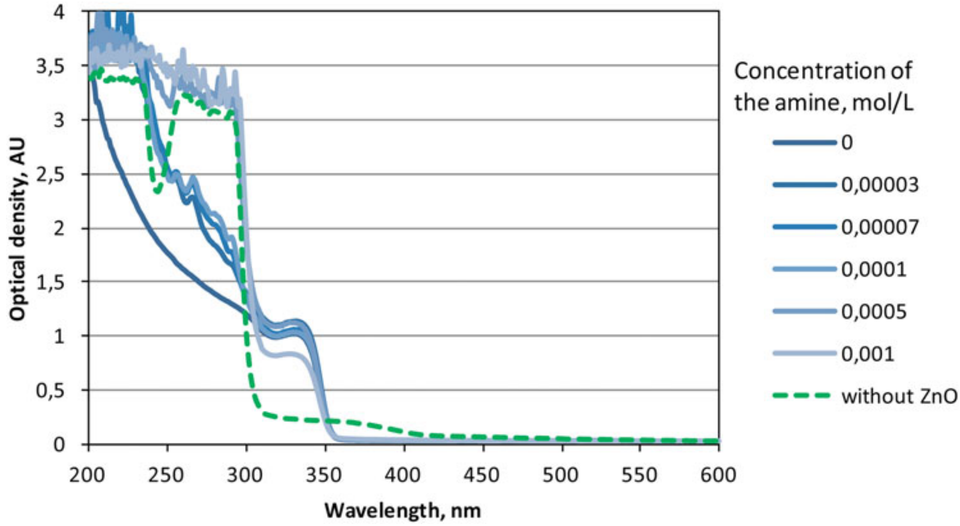

Figure 8. Absorption spectra of ZnO in the presence of tryptamine. [ZnO] = $2{\cdot}10^{-3}$ mol/L.

of the films decreases with the increase of concentration of the amines. The most significant increase of the luminescence intensity is observed for dopamine. Therefore, it is promising to use such films for freshness/spoilage detection of a packaged product by the change of photoluminescence intensity while possibly exploiting antimicrobial, photovoltaic and piezoelectric properties of nano-ZnO.

It is important to determine the mechanism of luminescence quenching of nano-ZnO films in contact with dopamine, tyramine, tryptamine, and histamine. This can be achieved with the anaylsis of absorption spectra of the samples. Contrary to the situation with dopamine, with the increase of the concentration of the other amines in the

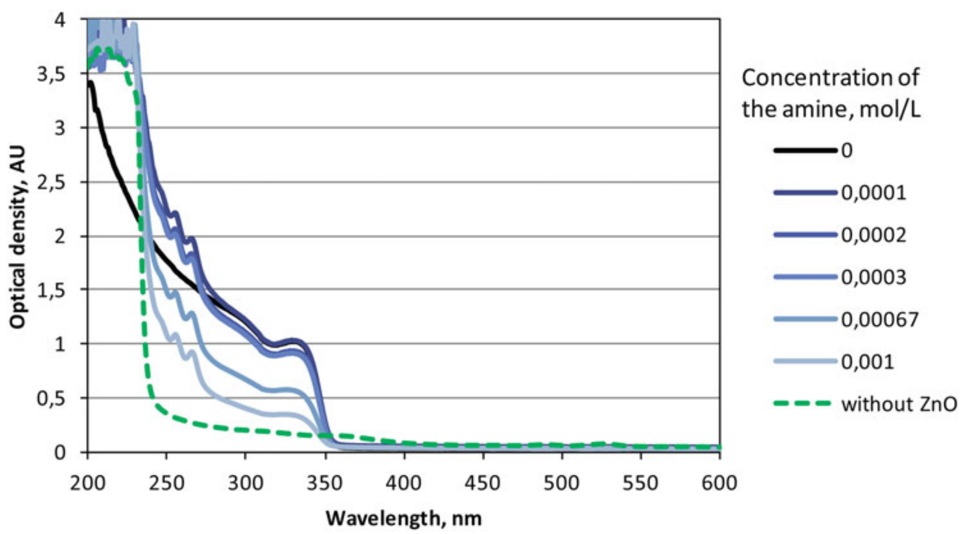

Figure 9. Absorption spectra of ZnO in the presence of histamine. [ZnO] = $2{\cdot}10^{-3}$ mol/L.

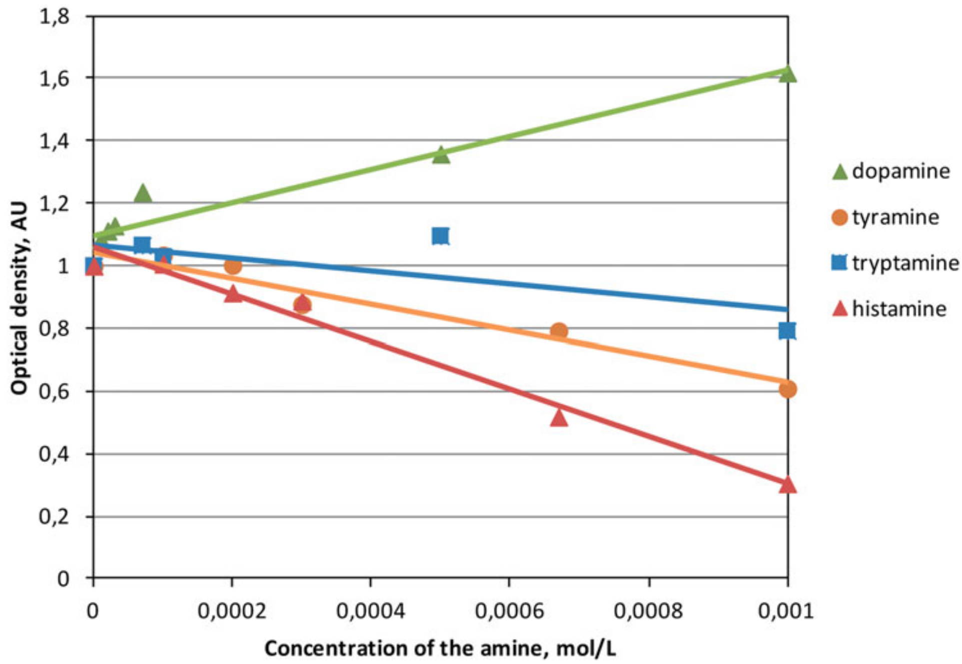

Figure 10. The change of optical density of nano-ZnO films depending on concentration of the amines. [ZnO] = $2{\cdot}10^{-3}$ mol/L.

system, it absorbs light in UV region of the spectrum less intensively (Fig. 7, Fig. 8, and Fig. 9).

Unlike the situation with dopamine, a significant decrease of the intensity of the luminescence with the increase of the concentration of the amine can not be explained by intensive absorption of the system in the UV region of the spectrum (Fig. 7, Fig. 8, and Fig. 9) as the intensity of absorption decreases at concentration of the amines 10^{-3} mol/L. Formation of non-luminescent complexes of histamine with nano-ZnO can be accounted for the decrease of the intensity of the luminescence.

The change of optical density of nano-ZnO films in the presence of the amines is shown in Fig. 10 for absorption data at 340 nm.

The increase of the optical density of nano-ZnO films in the presence of dopamine and the decrease of it in the presence of other amines (tyramine, tryptamine, and histamine) can be clearly distinguished.

Conclusions

It was determined that nanosized luminescent systems containing ZnO are promising for usage in "intelligent" packaging due to the fact that intensity of luminescence of nano-ZnO films changes accordingly to the change of concentration of compounds which indicate decay processes in packaged food such as amines. ZnO nanocrystals were obtained in colloidal solution, the process of stabilization of nano-ZnO with oil varnish and polyvinyl acetate dispersion was studied, nano-ZnO films were deposited onto polymer surfaces by ink-jet and screen printing. The interaction of nano-ZnO films with dopamine, tyramine, tryptamine and histamine was investigated, and the correlation between intensity of photoluminescence of ZnO and concentration of the amines was determined.

The investigation of interaction of luminescent hybrid nanocomposites with packaged products and compounds indicating food spoilage or decay allowed developing multifunctional nanocomposites for active and "intelligent" packaging with anti-microbial, forgery-proof, and product quality detection properties by the change of luminescence intensity.

In the process of creating new varnish and ink compositions for smart packaging with nanosized ZnO for ink-jet, flexographic, pad (indirect gravure), or screen printing techniques the interaction of the functional components of such systems with the components of inks or varnishes and possible interference with performance of nanophotonic and photocatalytic systems should be taken into account. Another important issue is safety of all the components of freshness/spoilage detection system for smart packaging due to the fact that it comes into direct contact with packaged food.

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