

Printed luminescent coverings based on nanosized ZnO for active and intelligent packaging

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Received November 25, 2013

There were investigated luminescent coverings based on ZnO nanoparticles, which change luminescence intensity in contact with compounds that indicate decay processes of food products, for active and intelligent (smart) packaging. High luminescent transparent films were developed based on colloidal suspension of ZnO and polyvinylpyrrolidone (PVP) with different molecular mass, concentration of nano-ZnO, and film thickness in order to optimize the content of the compositions for enhancing their luminescence. The luminescent properties of films with different water solubility eliminating covers were studied. The water insoluble composition was obtained from ZnO nanoparticles stabilized with colloidal silicon dioxide and PVP in poly(methyl methacrylate), and the luminescent properties of films were studied. The compositions are safe for food packaging applications and can be applied to surfaces with flexography, inkjet, screen, and pad printing.

Исследованы люминесцентные покрытия на основе наночастиц ZnO, которые изменяют интенсивность люминесценции в контакте с соединениями, свидетельствующими о процессах распада пищевых продуктов, для активной и умной упаковки. Разработаны высоколюминесцентные прозрачные пленки на основе коллоидного раствора ZnO и поливинилпирролидона (ПВП) с различной молекулярной массой, концентрацией наночастиц ZnO и толщиной пленки с целью оптимизации содержания композиций для увеличения их люминесценции. Изучены люминесцентные свойства пленок с различными покрытиями, устраняющими растворимость в воде. Получены нерастворимые в воде композиции, содержащие наночастицы ZnO, стабилизированные коллоидным диоксидом кремния и ПВП в полиметилметакрилате, и изучены люминесцентные свойства пленок. Композиции являются безопасными для применения в пищевой упаковке и могут быть нанесены на поверхности с помощью флексографии, струйной, трафаретной и тампонной печати.

Друківані люмінесцентні покриття на основі нанорозмірного ZnO активних і розумних упакувань. О.О.Сарапулова, В.П.Шерстюк.

Досліджено люмінесцентні покриття на основі наночастинок ZnO, які змінюють інтенсивність люмінесценції в контактi із сполуками, що свідчать про процеси розпаду харчових продуктів, для активних і розумних упакувань. Розроблено високолюмінесцентні прозорі плівки на основі колоїдного розчину ZnO і полівінілпіролідону (ПВП) з різною молекулярною масою, концентрацією нано-ZnO і товщиною плівки з метою оптимізації вмісту композицій для збільшення їх люмінесценції. Вивчено люмінесцентні властивості плівок з різними покриттями, що усувають розчинність у воді. Отримано нерозчинні у воді композиції, що містять наночастинок ZnO, стабілізовані колоїдним діоксидом кремнію та ПВП у поліметилметакрилаті, і вивчено люмінесцентні властивості плівок. Композиції є безпечними для використання у харчових упакуваннях і можуть бути нанесені на поверхні за допомогою флексографії, струмінного, трафаретного і тампонного друку.

1. Introduction

Semiconductor nanoparticles, due to a number of specific properties that significantly distinguish them from the bulk materials of the same chemical composition, have been intensively studied as promising components of new functional materials with predetermined properties. These materials may find use in a variety of devices, including ultraviolet and visible optical screens, fluorescent markers, antibacterial coatings, luminescent solar concentrators, luminescent inks for security printing, smart packaging etc. The use of so-called active and intelligent, or smart packaging, which inform consumers about the quality and safety of a packaged food product consumption, is becoming more and more popular in recent years. Such systems are based on the functionality of an external or internal sensor which changes its properties depending on the internal or external environment and informs the consumer by changing optical, mechanical, electronic or other properties [1]. Thus, the creation of materials responsive to the changes in quality of packaged food products by changing luminescent properties is a relevant and promising task. However, such systems as coatings must be placed into direct contact with a packaged food product, which leads to a concern about the migration of components of the coating into the product. Therefore, these components must be safe for consumption in small quantities. Consequently, the use of fluorescent substances such as CdS, CdSe, CdTe etc., which are toxic, is impossible. On the other hand, materials such as luminescent ZnO nanoparticles attract attention as possible components for smart packaging systems due to their non-toxicity [2], antimicrobial properties [3], UV filtering properties [4] to prevent the undesired influence of light. An additional advantage of nano-sized ZnO is the ability to change the intensity of its luminescence emission in contact with substances that emerge in food product during storage [4], thus, coatings, which are composed of nanoparticles of ZnO, can be used to create a luminescent sensors for smart packaging.

ZnO nanoparticles usually lose their luminescent properties as a result to introduction of them into a polymer for subsequent formation of films or coverings on the surface of packaging materials. Moreover, high luminescent stable ZnO nanocrystals has been obtained in a limited range of solvents

(ethanol, isopropanol, dimethylformamide, etc. [5]), which put restrictions to possible macromolecular compounds to use in the compositions. Besides, the polymer has to be safe for consumption in small amounts and do not interact chemically with a packaged food product. It is essential to stabilize nanocomposites in solid condensed phase and apply luminescent nano-ZnO films for their subsequent use in active and intelligent packaging systems. Considering that, optimization of luminescent compositions and conditions for the application of the compositions to surfaces are required to be carried out, as there are factors that have influence on the luminescent characteristics and the luminescence intensity of films which are made of colloidal solutions containing zinc oxide nanocomposites.

The aim of this work was the formation of luminescent films based on nano-sized ZnO for subsequent use in active and intelligent (smart) packaging, the study of the influence of the conditions of formation of these films on their luminescence properties, investigation of the possibility of stabilizing surfaces of films based on PVP and nanosized ZnO, and the search of possibilities to incorporate ZnO nanoparticles into other more resistant to external conditions polymers, in particular poly(methyl methacrylate).

2. Experimental

ZnO nanoparticles in ethanol were obtained from zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), sodium hydroxide (NaOH), and 100 % ethanol ($\text{C}_2\text{H}_5\text{OH}$) [5]. Polyvinylpyrrolidone (PVP) was added to the ZnO colloidal solution in ethanol (concentrations $2 \cdot 10^{-3}$, $1 \cdot 10^{-2}$ and $2 \cdot 10^{-2}$ mol/L) at room temperature and stirring (molar mass 10000, 40000 and 360000 g/mol) to obtain PVP concentration of 10 % and 25 % in solution). The mixture was stirred until complete dissolution of the polymer, after that the composition was uniformly distributed on a glass substrate (with different film thicknesses) and dried at room temperature. To obtain coverings with ZnO nanoparticles in poly(methyl methacrylate) (PMMA), silicon dioxide and PVP were added to colloidal ZnO nanocrystals in ethanol, and the resulting solution was mixed with PMMA solution in 1,2-dichloroethane at room temperature and vigorous stirring. Then the compositions were deposited onto glass surfaces and left to dry at room temperature.

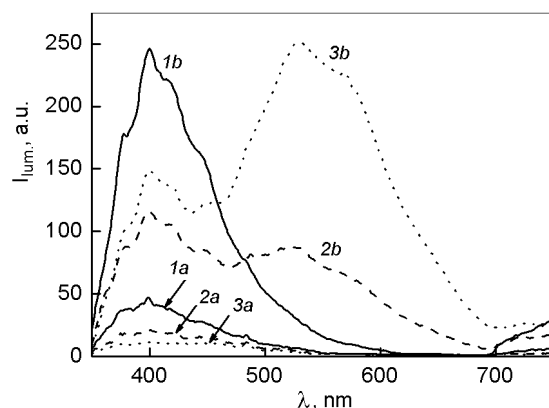


Fig. 1. Influence of molar mass of PVP on the luminescence intensity of the films. 1 — $M(\text{PVP}) = 10000$ g/mol, 2 — $M(\text{PVP}) = 40000$ g/mol, 3 — $M(\text{PVP}) = 360000$ g/mol, a — samples without ZnO, b — $[\text{ZnO}] = 2 \cdot 10^{-2}$ mol/L, $\lambda_{ex.} = 330$ nm.

The photoluminescence spectra were recorded with a fluorescence spectrometer (Perkin Elmer, LS 55) and excited with light with wavelength of 330 nm. The absorption spectra (optical density) were recorded with a spectrophotometer (Analytik Jena, Specord 210).

3. Results and discussion

It has been found that the introduction of nano-ZnO to poly(methyl methacrylate), polyvinyl alcohol (PVA), and gelatin leads into the loss of luminescent properties, and only with the use of PVP can stable luminescent compositions retain luminescent properties after application to the surface and evaporation of the solvent. It is important that PVP is safe and used in the food industry as a food additive E1201, as well as in medical practice PVP solutions are known as temporary blood substitutes. Another advantage of PVP is the fact that PVP allows obtaining transparent coatings. Therefore, the formation of films of ZnO nanoparticles in PVP and the influence of several factors on the luminescence intensity of these films were investigated.

Fig. 1 shows the effect of molar mass of PVP on the luminescence intensity of films without nano-ZnO and with the addition of nano-ZnO. The samples without ZnO nanoparticles exhibit a small band luminescence (at 400 nm) which decreases with the increase of molar mass of PVP (Fig. 1, curves 1a, 2a, 3a). After the introduction of nano-ZnO into the polymer the luminescence intensity of the samples in the area of emis-

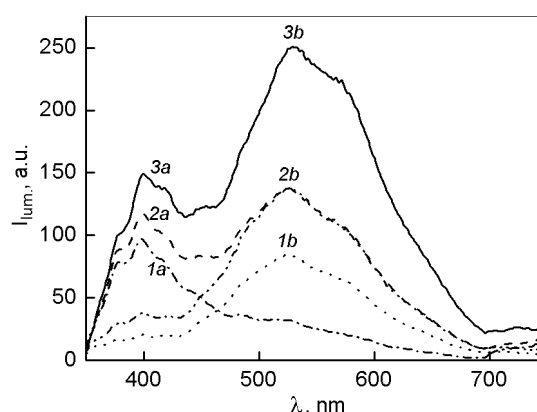


Fig. 2. Influence of the initial concentration of colloidal ZnO on the luminescence intensity of the films. 1a — $[\text{ZnO}] = 2 \cdot 10^{-3}$ mol/L, 2a — $[\text{ZnO}] = 1 \cdot 10^{-2}$ mol/L, 3a — $[\text{ZnO}] = 2 \cdot 10^{-2}$ mol/L, film thickness 500 μm ; influence of the thickness (number of layers) of PVP films containing nanosized ZnO on the luminescence intensity, $[\text{ZnO}] = 2 \cdot 10^{-2}$ mol/L. 1b — 1 layer (100 μm), 2b — 2 layers (200 μm), 3b — 5 layers (500 μm), $\lambda_{ex.} = 330$ nm, $M(\text{PVP}) = 360000$ g/mol.

sion of ZnO (525 nm) increases with the increase of molar mass of PVP (Fig. 1, curves 1b, 2b, 3b). Thus the appearance of distinct peaks in the area of luminescence emission of the polymer (at 400 nm) in the curves 1b, 2b, 3b is most likely a result of participation of functional groups at the ends of the polymer chains of PVP in radiative processes in the polymer, as well as effective capture of electronic excitation of ZnO nanoparticles by ending groups, followed by radiation in the natural radiation region of the polymer. With the decrease of molar mass of the polymer (down to 10000 g/mol), total amount of individual polymer chains per unit weight of PVP increases, therefore total amount of functional groups, which are situated at the ends of polymer chains, per unit weight of PVP increases too; this leads to the reduction of the luminescence band in the area of nano-ZnO emission (525 nm) and the increase of luminescence intensity in the area of PVP radiation (400 nm).

Therefore, to obtain maximum intensity of luminescence of films in the long wavelength region (which is characteristic of nanocrystalline ZnO), it is optimal to use PVP with the highest molar mass ($M = 360000$ g/mol). It has been shown in Fig. 1 that changing the molecular weight of PVP allows varying color of luminescent emis-

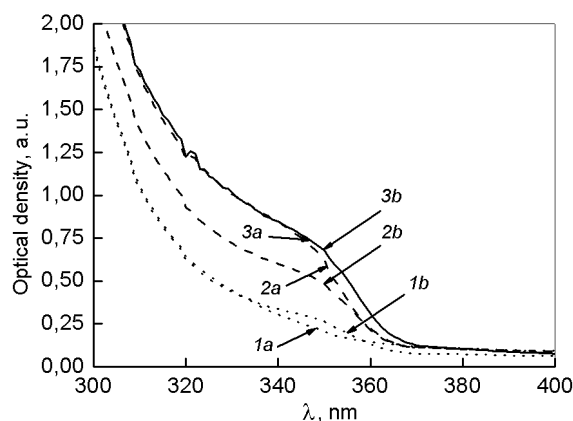


Fig. 3. Influence of the initial concentration of colloidal ZnO on the absorbance spectra of the films. *1a* — $[\text{ZnO}] = 2 \cdot 10^{-3}$ mol/L, *2a* — $[\text{ZnO}] = 1 \cdot 10^{-2}$ mol/L, *3a* — $[\text{ZnO}] = 2 \cdot 10^{-2}$ mol/L, film thickness 500 μm ; influence of the thickness (number of layers) of PVP films containing nanosized ZnO on the absorbance spectra, $[\text{ZnO}] = 2 \cdot 10^{-2}$ mol/L. *1b* — 1 layer (100 μm), *2b* — 2 layers (200 μm), *3b* — 5 layers (500 μm), $M(\text{PVP}) = 360000$ g/mol.

sion of the films from blue to green and yellow, which may be appropriate for creating systems with different colors of luminescent emission for active and intelligent packaging.

With the increase of concentration of ZnO nanoparticles luminescence intensity of PVP films in the region of nano-ZnO emission (525 nm) increases proportionally with the increase of nanoparticle concentration (Fig. 2, curves *1a–3a*).

Consequently, it is appropriate to use the highest concentration of ZnO nanocrystals in ethanol, which is limited to $2 \cdot 10^{-2}$ mol/L [5].

It is important to study the effect of film thickness of PVP containing nano-ZnO on the luminescence intensity of films, for the usage of printing techniques for application of films to surfaces. As can be seen from Fig. 2 (curves *1b–3b*), in order to increase the luminescence intensity of the films film thickness of the coating layer should be increased. For this purpose the use of printing techniques (screen printing, flexography, inkjet, pad printing etc) would be convenient.

Fig. 3 displays the absorbance spectra of the films for different concentrations of ZnO nanoparticles (curves *1a–3a*). It can be seen from Fig. 3 that with the increase of concentration of ZnO nanoparticles in PVP films there is a shift in the edge of ab-

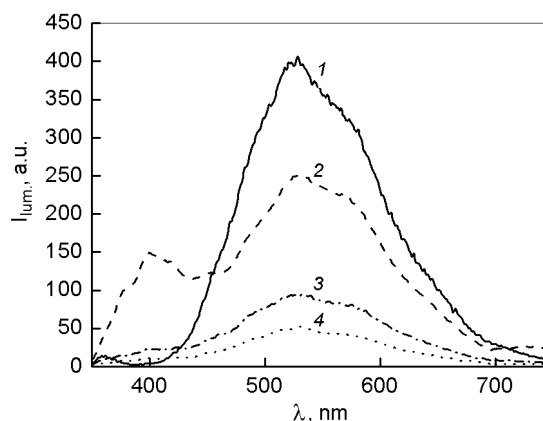


Fig. 4. Luminescence of ZnO nanoparticles in colloidal solution (*1*), uncoated films containing ZnO nanoparticles and PVP (*2*), and films coated with 1 % PVA solution (*3*) and 10 % PVA solution (*4*), $[\text{ZnO}] = 1.33 \cdot 10^{-2}$ mol/L, $\lambda_{ex.} = 330$ nm.

sorption band to the long wavelength region of the spectrum, which indicates increase in size of ZnO nanoparticles. Fig. 3 also shows the absorbance spectra of the films for different concentrations of ZnO nanoparticles (curves *1b–3b*). Similarly to the luminescence intensity, with the increase of concentration of ZnO nanoparticles absorbance intensity of PVP films in the UV region of spectrum increases proportionally with the increase of nanoparticle concentration.

Water solubility of PVP makes its films not suitable for usage in contact with foods which contain water. The way to overcome this difficulty can be the usage of a thin coating layer of some polymer material. It has been discovered that the use of such coatings as polyurethane or butyl acetate leads to complete quenching of luminescence. PVA is a water soluble polymer, however, after drying it becomes insoluble in water due to the formation a network structure. The effect of the coating of PVA on the intensity of the luminescence of zinc oxide films in PVP was studied. For varying coating thickness PVA solutions with different concentrations were applied to the surface of the films based on ZnO in PVP using "dip-coating" technique. Adjustment of coating thickness can be carried out more conveniently using printing techniques. According to Fig. 4 (curves *3* and *4*), PVA coating leads to significant luminescence quenching. However, with reduction of PVA concentration (hence coating thickness) luminescence quenching of the films can be reduced too. Therefore, it is appropriate to

use thin layers of PVA coating of the films if they are to be placed in contact with water.

As the use of PVA coatings for obtaining water insoluble luminescent films leads to deterioration of luminescent properties of the films, the possibilities of stabilization of ZnO nanoparticles for the subsequent introduction of them into some water-resistant polymers were considered. In particular, the results were obtained which indicate the prospects of stabilizing ZnO nanoparticles with silicic acid anhydride and PVP with following introducing them to PMMA. For this purpose colloidal ZnO nanocrystals in ethanol were introduced to PVP and silicic acid anhydride, and the resulting solution was mixed with PMMA solution in 1,2-dichloroethane with vigorous stirring at room temperature. The prerequisite of preserving luminescent properties of ZnO nanoparticles in PMMA in our study was the simultaneous presence of silicic acid anhydride and PVP as stabilizers of nano-ZnO. The absence of silicic acid anhydride or PVP in the system resulted in complete suppression of luminescence of ZnO nanoparticles after drying PMMA film. This synergistic effect can be explained by better stabilization of the surface defects of ZnO nanocrystals, adsorbed in the pores of silicic acid anhydride.

The luminescence spectra of films, obtained from compositions of nano-ZnO stabilized with silicic acid anhydride and PVP in PMMA and dichloroethane, are shown in Fig. 5. The concentration of ZnO nanocrystals in ethanol varied.

With the increase of concentration of ZnO nanoparticles in the composition from $6.67 \cdot 10^{-3}$ mol/L to $1.33 \cdot 10^{-2}$ mol/L, the maximum luminescence intensity of ZnO nanoparticles (at 520 nm) increases from 100 (Fig. 5, curve 3) and 200 (Fig. 5, curve 4) to 600 arb. units (Fig. 5, curve 5). It is worth noting that the last value is 1.5 bigger than the luminescence intensity of nano-ZnO stock solution in ethanol (Fig. 5, curve 1) and 2.4 bigger than the luminescence intensity of uncoated films containing nano-ZnO and PVP (Fig. 5, curve 2), which can be attributed to partial aggregation of ZnO nanoparticles in colloidal solution or PVP film. Due to quantum size effects, in particular the dependence of the allowed bands of the semiconductor to its size, there is a size distribution in such systems, therefore charge separation between nanoparticles of different sizes is possible. This ef-

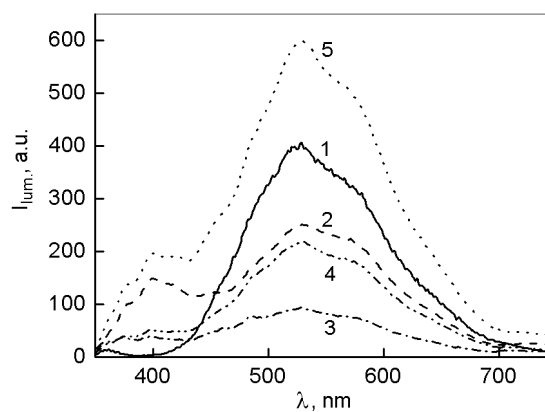


Fig. 5. Effect of the concentration of ZnO nanoparticles, stabilized by silicic acid anhydride and PVP in PMMA on the luminescence intensity of films, 1 — luminescence of ZnO nanoparticles in solution, $[ZnO] = 1.33 \cdot 10^{-2}$ mol/L; 2 — uncoated films containing ZnO nanoparticles and PVP, $[ZnO] = 1.33 \cdot 10^{-2}$ mol/L; 3 — $[ZnO] = 6.67 \cdot 10^{-3}$ mol/L, 4 — $[ZnO] = 1 \cdot 10^{-2}$ mol/L, 5 — $[ZnO] = 1.33 \cdot 10^{-2}$ mol/L, $\lambda_{ex.} = 330$ nm.

fect reduces luminescence intensity. However, the presence of silicic acid anhydride in the composition allows ZnO particles to be distributed over its surface and pores and avoid contact between each other, which results in the increase of luminescence intensity up to 2.4 times.

4. Conclusions

Luminescent films based on nanosized ZnO are quite promising for the usage in active and intelligent (smart) packaging. In this study, optimal composition and parameters of application of luminescent compositions that contain nano-ZnO and PVP to surfaces were developed on the basis of the study of the influence of molar mass and concentration of PVP, concentration of ZnO nanoparticles, and layer thickness of the films. There have been also investigated the possibility of coating of luminescent films based on ZnO nanoparticles and water soluble PVP in order to eliminate their water solubility to expand their possible scope of application. It has been found that thin layer of 1 % PVA solution in water has the least significant effect on the luminescence intensity of the investigated films.

In order to obtain insoluble in water highly luminescent films the composition has been developed by means of stabilizing ZnO nanoparticles with the silicic acid anhydride and PVP with following introducing them into PMMA. On the basis of

the study of luminescent properties of the films the optimal composition of the components was developed.

Luminescent compositions based on ZnO nanoparticles can be applied to packaging materials such as polypropylene film to obtain coverings, therefore creating active and intelligent (smart) packaging which informs consumers of safety of consumption of a packaged food product by varying the luminescence intensity of the coverings. It would be convenient to use printing techniques such as flexography, screen, inkjet, and pad printing for application of the compositions to packaging materials due to high-productivity of these techniques, as

well as their ability to manipulate film thickness.

Acknowledgements. This investigation was supported by the State Fund for Fundamental Researches of Ukraine (grant F54.2/005).

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