Influence of Parameters of Screen Printing on Photoluminescence Properties of Nanophotonic Labels for Smart Packaging

Olha Hrytsenko, Vitaliy Shvalagin, Galyna Grodziuk, and Vasyl Granchak

1 Institute of Publishing and Printing, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", 1/37 Yangel Str., Kyiv 03056, Ukraine
2 L. V. Pisarzhevskii Institute of the Physical Chemistry, The National Academy of Science of Ukraine, 31 Nauky Ave., Kyiv 03028, Ukraine

Correspondence should be addressed to Olha Hrytsenko; olhasarapulova@gmail.com

Received 30 October 2016; Revised 13 January 2017; Accepted 18 January 2017; Published 14 February 2017

Academic Editor: Marco Rossi

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Smart packaging is becoming more popular on world market as a new type of packaging able to react to changes in a packaged product during storage and informs a customer about the safety of consumption of packaged food. This article investigates the main technological issues of the use of nanophotonic printing inks based on ZnO/SiO₂ nanoparticles and polyvinylpyrrolidone (PVP) for printing active elements of smart packaging on paper substrates, concerning material properties and parameters of screen printing. It is determined that the use of ink compositions with medium content of ZnO/SiO₂ nanoparticles allows obtaining blue-green and blue shades of luminescence color of screen printed images by changing ink layer thickness on papers with different contents of optical brightness agents (OBAs). The minimum content of ZnO/SiO₂ nanoparticles in the developed fluorescent inks leads to blue luminescence colors regardless the contents of OBAs in the selected paper. The luminescence intensity is directly proportional to ink layer thickness and partly depends on the content of OBAs in the selected paper. In order to fabricate nanophotonic elements of smart packaging with predetermined photoluminescence properties, the influence of investigated factors on photoluminescence properties of printed nanophotonic labels should be taken into account.

1. Introduction

Smart packaging and intelligent packaging as its subgroup are becoming increasingly popular in the world [1, 2]. It is determined as a package with an internal or external system (sensor or indicator) for providing information on storage history and/or quality of a packaged product [3]. Smart packaging is unique because of its ability to recognize and report the status of a packaged product and, therefore, its safety for consumption. It is known that expiration date on a packaging is no guarantee that the product was kept in storage under the correct conditions (temperature, moisture, light exposure, defrosting and refreezing, etc.). A chemical sensor that analyzes actual information about food content, however, could reliably prevent food poisoning.

There is a wide variety of methods for fabricating smart packaging, depending on the functionality of a sensor. There are optical oxygen sensors and indicators [4, 5], which employ the principle of luminescence quenching or color changes caused by the contact with target substances. Optical oxygen indicators could be applied to packaging by printing techniques [6]. Oxygen sensors can also be placed on a packaging as a label or laminated into a packaging material (polypropylene film) [7]. Similar principles could be employed for production of carbon dioxide sensors [8]. There are plenty of freshness/spoilage indicators [9–11], optical biosensors for indicating microorganisms and gases that indicate decay processes in packaged food products. Other systems for smart packaging are time/temperature indicators [12–15], applied to a package surface by printing techniques or as separate labels. These indicators change color according to the age of the product, considering the storage temperature. However, they do not analyze the actual state of the product inside the package.
Analytical and informative function of packaging can be effectively provided by printing special image with nanophotonic elements onto the packaging surface [16]. Nanophotonic elements, such as zinc oxide (ZnO) nanoparticles and its nanocomposites, are safe in contact with food, possess antimicrobial properties [17,18], absorb UV radiation [16,19], and are able to change their photoluminescence parameters (color, intensity) according to the deterioration processes in a packaged product as a result of the reaction to the presence of substances that occur in food products during spoilage processes [20,21]. Such changes could be visually controlled by a customer, who will be confident in product quality and safety.

Production of printed labels is possible using traditional printing techniques which allow obtaining thick layers of ink on a substrate. Screen printing is one of the most perspective printing techniques for such purposes [22], which can provide low-cost production of printed labels on industrial scale. Rotary screen printing devices are compact and inexpensive; they can be installed in addition to existing production lines and deposit inks with nanophotonic elements onto smart food packaging. However, for the use in real printing process, the influence of technological factors on photoluminescence properties of the obtained printed layers should be considered in order to enhance the intensity of luminescence, manage its original color, and calculate further changes in luminescence properties of smart packaging elements on a smart packaging during its exploitation in contact with food products. These factors include content of ZnO/SiO₂ nanoparticles in printing ink, ink layer thickness, and optical properties of paper. The content of ZnO/SiO₂ nanoparticles in an ink composition could be regulated during ink preparation process. The thickness of an ink layer obtained by screen printing depends on many parameters: stiffness and edge parameters of a squeegee, squeegee angle during printing, squeegee pressure on a printing plate during printing, printing plate parameters (thickness of the mesh thread, mesh number), the value of the technological gap (distance between the mesh and the substrate), printing speed, ink viscosity, and so forth. In semiautomatic and automatic screen printing presses this thickness can be accurately set by setting the following technological parameters of a printing press: squeegee angle, squeegee pressure, and the value of the technological gap. The current study of the technological process of manufacturing of smart packaging with nanophotonic elements using screen printing technique will allow its industrial production.

2. Materials and Methods

Zinc acetate (Zn(CH₃COO)₂) and sodium hydroxide (NaOH) of pure grade were all obtained from Sigma-Aldrich (St. Louis, Missouri, United States) and were used without further purification. Hydrophobic silica (SiO₂) AEROSIL® R972 was supplied by Evonik (Essen, Germany). Ethanol was purchased from the State Enterprise “Ukrsprit” (Kyiv, Ukraine) with volume concentration of ethyl alcohol 96.3%. To remove water from the source ethanol, it was boiled for 4 h in heated calcium oxide (CaO) followed by distillation. CaO was purchased from Himlaborreaktiv Ltd. (Kyiv, Ukraine).

Colloidal solution of ZnO/SiO₂ nanoparticles in ethanol with concentration of ZnO 2 · 10⁻² mol/L was prepared according to the method described in [23] by alkaline hydrolysis of Zn(CH₃COO)₂ in dried ethanol. Samples of 0.183 g Zn(CH₃COO)₂ with 5 g SiO₂ and 0.064 g NaOH were separately dissolved in 45 and 5 mL of absolute ethanol, respectively. 1 g of SiO₂ per 10 mL of the resulting solution was used in order to achieve the maximum luminescence intensity [23]. Then the solutions were cooled to 0°C and mixed with vigorous stirring. After that, the mixture was maintained at 60°C for two hours. ZnO nanoparticles, obtained according by the aforementioned method, have crystalline nature, which is confirmed by XRD results, mentioned in [23], with peaks in the diffraction pattern, typical for hexagonal ZnO. The average size of obtained ZnO nanoparticles was 4.4 ± 0.75 nm.

The printing ink was created by diluting the obtained colloidal solution of ZnO/SiO₂ nanoparticles with ethanol, followed by addition of 12% of polyvinylpyrrolidone (PVP) M = 360,000 g/mol. The inks were obtained with concentration of ZnO nanoparticles 0.15%, 0.1% and 0.05%. The content of ZnO nanoparticles of 0.15% in the ink composition is maximum possible to obtain by direct dissolution of PVP in the obtained source solution of ZnO/SiO₂ nanoparticles in ethanol, which contained 2 · 10⁻² mol/L of ZnO nanoparticles [24]. Less concentration of ZnO nanoparticles in the ink composition (0.1% and 0.05%) was obtained by diluting the source colloidal solution of ZnO/SiO₂ nanoparticles with ethanol 1.5 for 3 times, respectively, followed by adding of 12% of PVP (m/m in ethanol solution of ZnO/SiO₂ nanoparticles). The use of PVP in 12% mass concentration provides the needed screen printing ink viscosity. Less viscosity leads to the incursion of excess ink onto a substrate through the printing elements of screen printing plates; higher viscosity hampers the process of ink deposition onto a substrate through a mesh of a screen printing plate, it leads to the formation of ink filaments, which causes defects in the resulting printed image. The viscosity of ink in this study is determined by content of PVP (12%) and it is constant in the experiment.

The coatings were obtained using screen printing of the produced nanophotonic compositions on paper substrates. 12 printed samples for each combination of technological parameters were prepared by two technicians; for each sample 5 measurements were taken. Student’s t-test was performed to validate the data; at a 95% confidence level, p value of <0.05 was considered statistically significant. To obtain printed solid areas 4 × 4 cm of different thickness, screen printing plates with different mesh were used (mesh #76 and #120), and the ink was deposited in 1, 2, 3, 4, and 5 layers in order to vary ink layer thicknesses in a range from 4 to 45 μm. Each subsequent layer was deposited after drying the previous ink layer under room temperature conditions without special equipment. This study indicates the final ink thickness, without reference to the quantities of technological factors affecting it. Ink layer thickness is determined individually for a specific printing equipment at each individual printing company. Ink thickness in this study was calculated by gravimetric method, by weighting the substrate before and after ink deposition.
Usually paper contains some kind of optical brightness agents (OBAs), which have their own luminescence. Three kinds of paper were selected which have the same surface smoothness (200 Bekk seconds), porosity (absorbing capacity, 2 mL/min), and thickness (540 μm) but different contents of OBAs (low, medium, and high contents of OBAs corresponding to brightness values of 45, 60, and 75% ISO, resp.).

The main investigated technological factors are content of ZnO/SiO$_2$ nanoparticles in printing ink, ink layer thickness on the substrate in solid state, and optical properties of paper (photoluminescence spectra as the indication of OBA content in paper). The investigated parameters of photoluminescence of the obtained printed layers are photoluminescence intensity and color. The photoluminescence color is determined by the correlation of the intensity and position of a photoluminescence band.

The instruments used to perform the experiments included laboratory chamber ThermoLab (ThermoLab Scientific Equipments Pvt. Ltd., Vasai, India), magnetic stirrer, and analytical scales Radwag XAS 220/C (Radwag Balances and Scales, Radom, Poland). Optical density of the suspensions was measured with a spectrophotometer Specord 210 (Analytik Jena AG, Jena, Germany). Photoluminescence spectra were recorded with a luminescence spectrometer LS55 (Perkin-Elmer, Waltham, Massachusetts, United States) and excited by light with the wavelength $\lambda_{\text{exc}} = 330$ nm. Conditions of the measurements are as follows: excitation slit 15 nm, emission slit 2.5 nm, scan speed 500 nm/min, and emission monofilter at 390 nm.

### 3. Results and Discussion

The luminescence spectrum of the obtained ZnO/SiO$_2$ composite in ethanol with a concentration of ZnO $2 \times 10^{-2}$ M is shown in Figure 1, curve 1. The luminescence spectrum of the ink composition with PVP in a liquid state is presented in Figure 1, curve 2. The addition of PVP does not change the luminescence properties of the colloidal solution drastically; the luminescence peak in the short wavelength area of the visible spectrum (at 400 nm) is characteristic of PVP and the reduction of the peak at 520 nm is explained by the decrease in concentration of ZnO/SiO$_2$ nanoparticles in the ink composition due to addition of the polymer (PVP).

OBAs in paper structure interfere with luminescence of a printed image and can even quench it completely. The presence of own luminescence of paper leads to visual distortion and even the complete visual disappearance of an image printed thereon with fluorescent inks. This phenomenon occurs because OBAs can have much greater luminescence intensity (usually in the short wavelength area of visible spectrum, 400–450 nm) than the luminescence intensity of the printed image. Therefore, non-OBA papers are recommended for security printing with fluorescent inks, or at least paper should have relatively low content of OBAs. Visually, such papers are less white; that is, they possess yellowish hue, leading to gradational distortions of printed images, visible in daylight. Taking this into account, the research of the impact of the content of optical brighteners in paper on luminescent properties of images printed with ink compositions with nanophotonic elements is crucial for the production process. The luminescence spectra of the selected papers are shown in Figure 2.

Figure 3 presents the photo of screen printed impressions obtained using the developed ink compositions containing ZnO/SiO$_2$ nanoparticles and PVP under ultraviolet (UV) light ($\lambda = 330$ nm) and daylight.

As can be seen in Figure 3, the developed ink compositions are invisible in daylight, which allows to use them not only for indication changes in food product state, but also for security printing purposes. Unlike organic phosphors, traditionally used for security printing, nano-ZnO is more
stable during time and maintains luminescent properties even after exposure to high temperature conditions (up to 100°C) and intensive light irradiation.

The luminescence spectra of images printed onto the paper with minimum content of OBAs (paper 1) and ink compositions with different contents of the fluorescent component are presented in Figure 4.

As it is shown in Figure 4, on paper with a minimum content of OBAs, the luminescence peak is in the short area of visible spectrum (\(\lambda = 430–440\) nm), partly caused by paper luminescence, partly by luminescence of PVP in ink compositions and luminescence of ZnO/SiO\(_2\) nanoparticles in this area of visible spectrum (see Figure 1). This peak decreases with decreasing the concentration of the fluorescent component, indicating that this peak is also caused by interaction of ZnO/SiO\(_2\) nanoparticles with PVP. In addition, in case of this paper, the use of the maximum concentration of ZnO/SiO\(_2\) nanoparticles in the ink composition causes luminescence peak in the area \(\lambda = 520\) nm, characteristic of ZnO nanoparticles. With the decrease of concentration of the fluorescent component, this peak decreases. For a more detailed study of these phenomena own luminescence spectra of ink compositions with ZnO/SiO\(_2\) nanoparticles and PVP, printed onto paper 1, have been calculated, by subtracting the intensity of luminescence of printed and unprinted areas of paper. They are shown in Figure 5.

Figure 5 illustrates that the reduction of fluorescent component in the ink composition printed on paper 1 does not change the peak in the short wavelength area and reduces the peak at \(\lambda = 520\) nm to its total disappearance.

Comparing the obtained results to previous studies [22], ink layers with ZnO/SiO\(_2\) nanoparticles as a luminescent component deposited onto paper substrates with the same ink layer thicknesses with the same concentration of nano-ZnO in the ink compositions demonstrate up to 2.5 times higher luminescence intensity at the same conditions of measurements, which corresponds to the difference between luminescence intensity of the initial colloidal solutions of ZnO nanoparticles and ZnO/SiO\(_2\) nanoparticles in ethanol [23].

Summary of changes in the luminescence peak at \(\lambda = 430\) nm and 520 nm is presented in Figures 6(a) and 6(b), respectively.

**Figure 3:** Screen printed impressions of the developed ink compositions under UV light (\(\lambda = 330\) nm) and daylight, respectively. [ZnO] = 0.15% and [PVP] = 12%.

**Figure 4:** The luminescence spectra of images printed onto the paper with the minimum content of OBAs (paper 1) using the ink compositions with the following contents of the fluorescent component (ZnO nanoparticles): (a) 0.15%; (b) 0.1%; (c) 0.05%.

**Figure 5:** Illustrates that the reduction of fluorescent component in the ink composition printed on paper 1 does not change the peak in the short wavelength area and reduces the peak at \(\lambda = 520\) nm to its total disappearance.
Figure 5: The own luminescence spectra of images printed onto the paper with the minimum content of OBAs (paper 1) using the ink compositions with the following contents of the fluorescent component (ZnO nanoparticles): (a) 0.15%; (b) 0.1%; (c) 0.05%.

For paper with a minimum content of OBAs, the dependencies for the luminescence peak at $\lambda = 430$ nm have nonlinear character, which means that, for each concentration of ZnO/SiO$_2$ nanoparticles, at some point the increase in ink layer thickness does not lead to the increase of the luminescence peak at $\lambda = 430$ nm. Such phenomenon can be used for color management of the ink layer, taking into account changes of the luminescence peak at $\lambda = 520$ nm. According to the calculations, ink layer thickness on the printed impressions and luminescence intensity at $\lambda = 520$ nm on paper 1 are significant to each other ($p$ values of 0.0014, 0.0034, and 0.0009 for concentrations of ZnO nanoparticles 0.05%, 0.1%, and 0.15%, resp.). The dependencies for the luminescence peak at $\lambda = 520$ nm have linear character, meaning that with the increase of ink layer thickness, possible for screen printing, the luminescence intensity in medium wavelength area of visible spectrum increases.

Similar phenomena are observed with increasing content of OBAs in paper as a printing material. The luminescence spectra of images printed onto the paper with the medium content of OBAs (paper 2) and ink compositions with different contents of the fluorescent component are shown in Figure 7.

The own luminescence spectra of images printed onto the paper with the medium content of OBAs (paper 2) using the ink compositions with the following contents of the fluorescent component are presented in Figure 8. Figure 8 illustrates that, as in the previous case, the luminescence peak at $\lambda = 520$ nm reduces with the decrease of the content of the fluorescent component. At the same time, the luminescence peak at $\lambda = 430$ nm increases, but in the case of medium and low concentrations of fluorescent component there is a partial absorption of paper luminescence in the short wavelength area of visible spectrum, probably by the fluorescent
Figure 6: The dependency of the luminescence peak at $\lambda = 430$ (a) and 520 nm (b) of printed impressions on paper with the minimum content of OBAs (paper 1), obtained using ink compositions with different contents of the fluorescent component (ZnO nanoparticles), on ink layer thickness.

Figure 7: The luminescence spectra of images printed onto the paper with the medium content of OBAs (paper 2) and ink compositions with the following contents of the fluorescent component (ZnO nanoparticles): (a) 0.15%; (b) 0.1%; (c) 0.05%.
component, as in Figures 8(b) and 8(c), the luminescence intensity values are negative in the short wavelength area of visible spectrum. With the increase of ink layer thickness on the impressions, such absorption decreases.

The described phenomenon can be seen in Figures 9(a) and 9(b), where the summary of changes in the luminescence peaks at \( \lambda = 430 \text{ nm} \) and 520 nm is shown, respectively, to the changes in ink layer thickness.

According to the calculations, ink layer thickness on the printed impressions and luminescence intensity at \( \lambda = 520 \text{ nm} \) on paper 2 are significant to each other (\( p \) values of 0.0045, 0.0169, and 0.0059 for concentrations of ZnO nanoparticles 0.05%, 0.1%, and 0.15%, resp.).

The luminescence spectra of images printed onto the paper with the maximum content of OBAs (paper 3) and ink compositions with different contents of the fluorescent component are shown in Figure 11. Figure 11 illustrates that, similarly to the previous cases, the luminescence peak at \( \lambda = 520 \text{ nm} \) decreases with the decrease of content of the fluorescent component in the ink compositions. The luminescence peak at \( \lambda = 430 \text{ nm} \) increases, but in the case of low concentrations of fluorescent component it remains practically unchanged.

The described phenomenon is illustrated in Figures 12(a) and 12(b), from the summary of changes in the luminescence peaks at \( \lambda = 430 \text{ nm} \) and 520 nm, respectively, to the changes in ink layer thickness.

According to the calculations, ink layer thickness on the printed impressions and luminescence intensity at \( \lambda = 520 \text{ nm} \) on paper 3 are significant to each other (\( p \) values of 0.0209, 0.0021, and 0.0244 for concentrations of ZnO nanoparticles 0.05%, 0.1%, and 0.15%, resp.).

Thus, Figures 5, 8, and 11 illustrate that regardless of the content of OBAs in paper, when using maximum concentrations of ZnO/SiO\(_2\) nanoparticles possible in ink compositions, by varying ink layer thickness on impression,
Figure 9: The dependency of the luminescence peak at $\lambda = 430$ (a) and $\lambda = 520$ nm (b) of printed impressions on paper with the medium content of OBAs (paper 2), obtained using ink compositions with different contents of the fluorescent component (ZnO nanoparticles), on ink layer thickness.

Figure 10: The luminescence spectra of images printed onto the paper with the maximum content of OBAs (paper 3) and ink compositions with the following contents of the fluorescent component (ZnO nanoparticles): (a) 0.15%; (b) 0.1%; (c) 0.05%.
green-yellow luminescence colors can be obtained (with significant excess of luminescence peak in the medium wavelength area over the peak in short wavelength area of visible spectrum) and green, blue-green, and blue colors can be obtained (with significant excess luminescence peak in the short wavelength area over the peak in medium wavelength area of visible spectrum). At medium and low concentrations of the fluorescent component in the ink composition, only blue-green and blue colors can be on a printed image.

The character of the dependencies of the luminescence peaks at $\lambda = 520$ nm on ink layer thickness of printed impressions with ZnO/SiO$_2$ nanoparticles in general corresponds to the character of the dependencies obtained for ink layers with ZnO nanoparticles as a luminescence component on paper and polymer substrates, discussed in [25]. Ink layer thickness on the printed impressions and luminescence intensity at $\lambda = 520$ nm on all the studied papers are found to be significant to each other, according to the calculations ($p$ value of $<0.05$). The presence of SiO$_2$ leads to much higher luminescence intensity of ink layers at $\lambda = 430$ and $\lambda = 520$ nm, which is crucial for visual registration of the response of printed labels for smart packaging to the changes in a packaged food product. Considering this fact, the use of the developed printing ink compositions will lead to more convenient exploitation of the manufactured printed elements by the customers, comparing to the ink compositions with ZnO nanoparticles, mentioned in [22, 25].

A comparison of the own luminescence spectra printed impressions on papers with different contents of OBAs (paper 1, paper 2, and paper 3 in the sequence of increase of OBAs...
Figure 12: The dependency of the luminescence peak at $\lambda = 430$ (a) and $\lambda = 520$ nm (b) of printed impressions on paper with the maximum content of OBAs (paper 3), obtained using ink compositions with different contents of the fluorescent component (ZnO nanoparticles), on ink layer thickness.

4. Conclusions

In this research, it is shown that ZnO/SiO$_2$ nanoparticles can be used for fabrication of active elements for smart packaging. Such elements are able to react to changes of a packaged product status by changes in luminescence color and intensity. The ink composition based on ZnO/SiO$_2$ nanoparticles and polyvinylpyrrolidone (PVP) was developed for screen printing. It was determined that optical properties of printing papers (which indicates the content of optical brightness agents) basically determine the luminescence colors that are possible to obtain, changing ink layer thickness of the printed images and the content of ZnO/SiO$_2$ nanoparticles in ink.
compositions. It was determined how to choose the paper, the concentration of the fluorescent component, and the thickness of ink layer to obtain blue, green, and yellow shades of luminescence color of printed images, fabricated with inks containing ZnO/SiO$_2$ nanoparticles. The results also allow obtaining printed images with nanophotonic elements with predetermined luminescence intensity. Such possibility of controlling the parameters of luminescence is of practical importance for the manufacture of functional labels for smart packaging for foodstuffs, as it will be possible to draw conclusions about the actual condition of packaged food product and therefore its suitability for consumption, based on the changes of luminescence intensity and color of a printed label.

**Competing Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**Acknowledgments**

Publications are based on the research provided by the grant support of the State Fund For Fundamental Research (Project no. F64/10-2015 from 28.03.16). The research was supported by the Ministry of Education and Science of Ukraine (Project no. 2873p).

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