FLUORESCENCE OF ZINC OXIDE IN POLYMERIC BINDERS

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Abstract

Doped zinc oxide colloids can exhibit photoluminescence. In printing industry, it is essential to prepare a feasible printing composition to gain a printable form of zinc oxide nanoparticles, which have good adhesion to the printing substrate. The study is focused on comparison of selected polymers (sodium carboxymethyl cellulose, polyvinylpyrrolidone, and 2-hydroxyethyl cellulose) used as binding agents and its influence on the colour and intensity of ZnO photoluminescence. Furthermore, optimal ratio of the binder: ZnO was studied. The spectral characteristics of zinc oxide layers in (or without) polymeric binders were analysed with UV-Vis spectrophotometry and fluorescence spectrophotometry. The homogeneity of deposited layers was characterised by image analysis using using ImageJ software.

Keywords: Zinc oxide, binders, photoluminescence, layers, spectra

1. INTRODUCTION

Zinc oxide (ZnO) is a n-type, wide band gap semiconductor which crystalizes in hexagonal wurtzite structure [1, 2]. ZnO is a promising material for development of solar cells, luminescent materials, light emitting devices, gas sensors, transparent electrodes, wave-guides, surface acoustic wave, and acoustic-acoustic devices [2, 3]. Research papers describe described various approaches for synthesising ZnO nanoparticles [4-9]. The fluorescence spectra of ZnO can be tailored by doping and depends on the particle size as well [10].

Copper doping of ZnO can evoke interesting optical, electrical, and ferromagnetic properties [2]. When doping ZnO with Cu atoms, the Zn^{2+} ions are substituted with Cu^{2+} ions in the ZnO host structure. Cu doping is therefore modifying the photoluminescence by creation of localized impurity levels [11, 12]. Furthermore, copper increases the intensity of deep trap emission of bulk ZnO and also the intensity of band gap emission of bulk ZnO.

In this study zinc acetate dihydrate was the starting compound for synthesis of Cu-doped ZnO. Monoethanolamine (MEA) accompanied with other solvents can be used to dissolve zinc acetate dehydrate [1, 13-16]. Alongside this, MEA is also used as stabilizer/capping agent which ensure highly oriented ZnO [13, 14]. The colloid used in this paper is in MEA solvent only. Higher boiling point of MEA requires addition of binding agents for obtaining dry films after deposition. For this reason, the porous structure of uncoated paper is well suited for fabrication of fluorescent films.

Indeed, we present application of fluorescent layers, where for ink composition, three types of binders, namely sodium carboxymethyl cellulose (CMC), polyvinylpyrrolidone (PVP), and 2-hydroxyethyl cellulose (2HEC) were used. Active fluorescent material, zinc oxide colloids doped with copper were added into the binder solutions and printed onto a Standard IGT Paper by screen printing technique.

2. EXPERIMENTAL

Materials and conditions. Laboratory-made zinc oxide doped with Cu (ZnO:Cu, 0.5 % of Cu) in monoethanolamine was synthesized from zinc acetate dihydrate ($(CH_3COO)_2Zn.2H_2O$, 99.0 %), copper acetate tetrahydrate ($(CH_3COO)_2Cu.4H_2O$, 98.0 %), and monoethanolamine ($NH_2CH_2CH_2OH$, 99.0 %). Polymers used as binding agents were sodium carboxymethyl cellulose (Mw ~ 250,000), 2-hydroxyethyl cellulose (Mw ~ 250,000), polyvinylpyrrolidon (K 90, Mw ~ 350,000), all purchased from Sigma-Aldrich.

Compounds were used as received without further purification. Paper used for printing was Standard IGT Paper which does not contain any fluorescent additives. Temperature in the laboratory during synthesis and printing was maintained between 20-25 °C and the relative humidity under 40 %.

Preparation of binder solutions. All polymers were supplied in powder form. The recommended concentration of binding solutions is around 10 mg/mL. All samples use distilled water as solvent. The zinc oxide is in form of solution which exploits MEA as solvent which hinders the possibility of creation of solid layers of ZnO. To ensure drying of the deposited layers, higher concentrations (50 mg/mL) of polymeric solutions were prepared. Thus, addition of smaller volume of binding solution was required which should not decrease the fluorescence of the sample in high extents due to decrease of ZnO concentration.

All powders were prepared in the same concentration. A weighed sample was inserted into required volume, the sample was then shook on a shaking device for 5 minutes. After first shaking, the sample was put into microwave oven for 5 second intervals repeatedly for 5 times or more (depending on the will to dissolve). Finally, the sample was put on a shaking device for 30 minutes to obtain a clear solution.

Introduction of ZnO into binder solutions. The ZnO colloid was introduced into the polymeric binders in 1 : 1 volume ratio and stirred vigorously for one day. The stirring had to be done at room temperature, because heating of the sample caused precipitation and inhibition of fluorescence.

Printing process. Printing of the prepared solutions was performed by screen printing (semi-automatic, Grafotechna, SP-B3) with a polyester mesh with mesh count 100 threads/cm. The gap between screen and substrate was 5 mm. Using smaller gaps, the substrate sticks on the screen due to high tack of the solution. The process of printing was performed by 2 passes of the squeegee without flooding before printing. For stronger emission, 5 layers were deposited onto the substrate. Layers were dried after each 2-pass print on a hot plate at 45 °C.

Measurements and conditions used. UV-Vis spectrometry was performed on Specord 210 (Analytic Jena). Emission spectra (excitation at 365 nm, unless provided otherwise) were measured with 1 nm resolution and constant photomultiplier voltage using Luminescence Spectrometer (Aminco Bowman Series 2). Thickness of layers was performed with mechanical thickness gauge (Schröder, Germany, accuracy 1 µm). ImageJ software (1.46r, Wayne Rasband, National Institutes of Health, USA) was used to determine the homogeneity of the deposited layers with plot profile function and surface roughness calculation plugin (by Gary Chinga and Bob Dougherty).

3. RESULTS AND DISCUSSION

From ZnO:Cu colloid, ink compositions were prepared (**Figure 1**). During introduction, the solution turned white and after stirring a clear ink composition was obtained. The colour of the ink compositions has slightly changed which was able to observe visually. The appropriate ratio between the binder solution and ZnO:Cu in MEA depends on two factors: preservation of highest intensity of fluorescence and the ability of the deposited film to dry. The volume : volume ratio of 1 : 1 was sufficient for dry film formation on the substrate.

The colloid and the binder solutions with ZnO:Cu content were analysed with UV-Vis spectrometry which shows the differences in absorbance spectra of the solutions as shown in **Figure 2** together with comparison of change in spectral distribution of fluorescence. Sample without polymeric binders shows one peak in the fluorescence spectra with a less pronounced shoulder on the right side. The peak with a shoulder is obvious for all samples with binders. Ink composition with PVP has the shoulder situated on the right side of the peak. On the other hand, ZnO:Cu in CMC and 2HEC binders show an inverse peak/shoulder distribution compared to that with PVP. In case of CMC and 2HEC ink compositions, the position of the peak in PVP ink composition acts as a shoulder, and at the position of its shoulder a peak is evident. This could have an effect on the colour difference between the samples which could be registered already in visible light. The intensity of fluorescence

in all three samples is very close to each other. This applies also to the printed samples shown in **Figure 3** but with a more obvious difference in case of 2HEC.

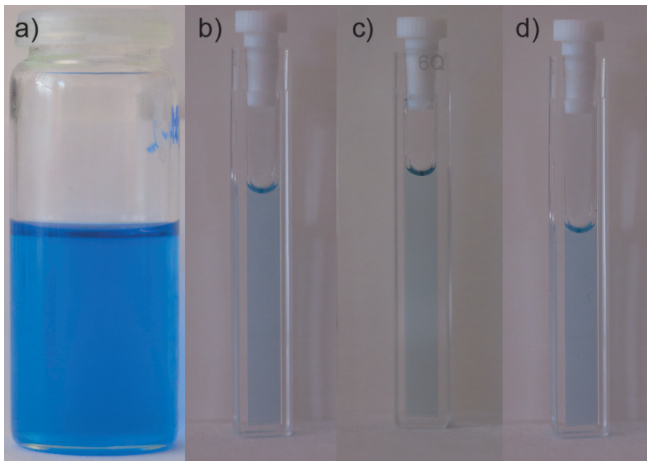

Figure 1 Photographs of a) ZnO:Cu colloid and its ink compositions with binders b) CMC, c) PVP, and d) 2HEC

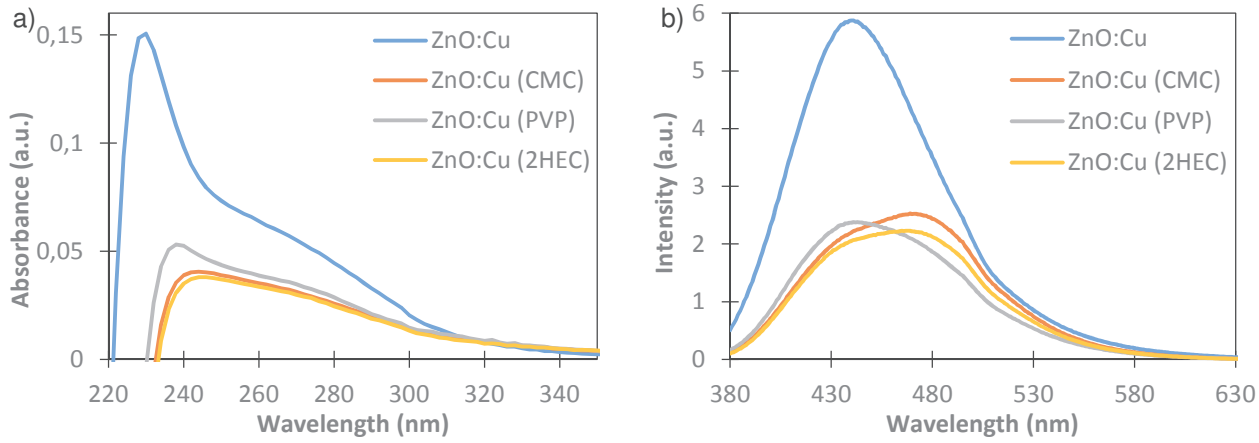

Figure 2 a) UV-Vis spectra and b) fluorescence spectra of starting colloid ZnO:Cu and its ink compositions with polymeric binders

First issue in printing of ZnO layers with binders was to find a proper method for depositing a solid layer without any bubbles caught in the layer. For this reason, the screen printing mesh must be positioned with a larger gap from the substrate. We have found that a 5 mm gap is sufficient. A flood stroke before printing was not used because the ink composition supposedly due its high cohesion formed a strong layer causing sticking of the substrate onto the mesh or formation of a foamy layer on the substrate. When using only one printing stroke, the layer contains air bubbles, which cannot escape from the layer. Therefore, two printing strokes were used. The first stroke was slow to force the highly viscous ink composition through the mesh and the second stroke was quick, used to improve the quality of the deposited layer. This 2-pass method was necessary to obtain a homogenous layer on the substrate.

After depositing a layer, the substrate was heated to 45 °C on a preheated plate. To maintain the same conditions for all deposited layers, the samples were dried after each deposition. Higher temperatures above 45 °C cause change of colour of the layers to brown tints, making the layers non-fluorescing or changing the fluorescence. The last deposited layer required longer period of drying, therefore all samples were dried overnight on the preheated plate. The final thicknesses of the printed layers are shown in **Table 1**. Standard

deviation of the paper thickness can be responsible for the differences of the layer thicknesses. Thickness of samples with CMC and PVP binders have similar thicknesses, the thickness of sample with 2HEC binder is lower by 2 µm which could contribute to the lower intensity of fluorescence.

Table 1 Thickness of substrate and thickness of 5 layers deposited on the substrate after drying

	Paper	ZnO:Cu (CMC)	ZnO:Cu (PVP)	ZnO:Cu (2HEC)
Thickness (µm)	142.4 ± 0.8	17.2 ± 0.8	17.4 ± 1.0	15 ± 0.8

The photographs of fluorescent films under UV-light lamp (365 nm) are shown in **Figure 3.** For estimation of the homogeneity a profile plot was used where the whole printed pattern is averaged. Surface roughness characterisation of the samples is shown in **Table 2**. Highest homogeneity and intensity of fluorescence can be observed in the case of CMC as binder. PVP causes an inhomogeneous film due to formation of clusters on the paper substrate. This effect was evident already during print, when the printed pattern could not be printed as a solid homogenous layer.

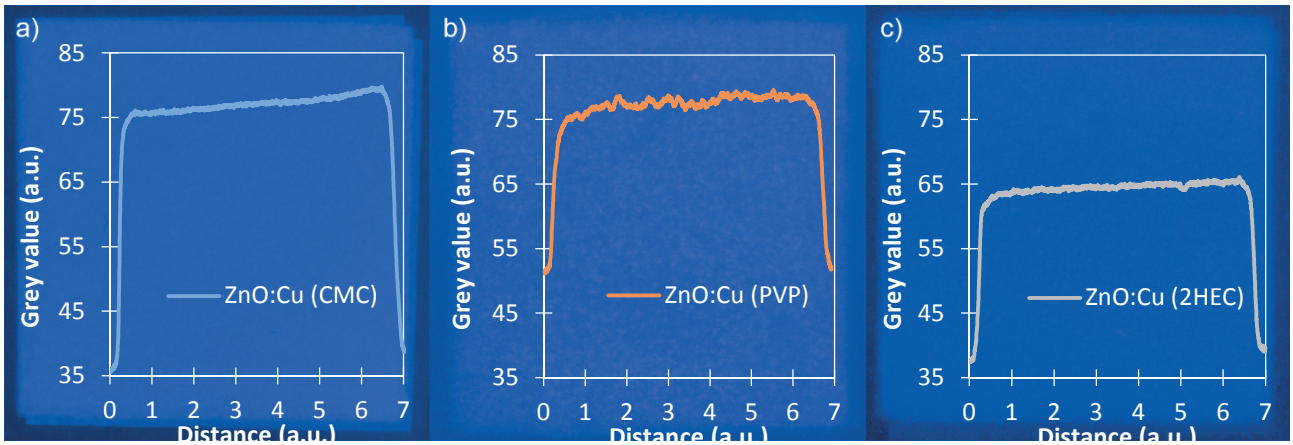

Figure 3 Printed samples of ZnO:Cu in a) CMC, b) PVP, and c) 2HEC binder with averaged profile plots of the samples as representation of the homogeneity of deposited films

Furthermore, on the edges of the printed layers, it can be seen that except the case of CMC binder, the edges are blurred which could mean that the solvent (water or MEA) penetrated into the structure of the paper and causes the bleeding effect. The sharpest edges of the print can be observed when CMC was used, then PVP, and the blurriest edges were found when 2HEC was used.

Table 2 Surface roughness evaluation of solid surfaces of samples in **Figure 3**. R_q: Root mean square deviation, R_a: Arithmetical mean deviation, R_{ku}: Kurtosis of the assessed profile, R_{sk}: Skewness of the assessed profile, R_v: Lowest valley (given by the min measurements), R_p: Highest peak (given by the max measurements), R_t: The total height of the profile.

Sample	R_q (a.u.)	R_a (a.u.)	R_{sk} (a.u.)	R_{ku} (a.u.)	Highest Peak (a.u.)	Lowest Valley (a.u.)	Total height (a.u.)
ZnO:Cu (CMC)	77.3	77.4	1.0	1.0	112.3	48.7	161.0
ZnO:Cu (PVP)	77.9	77.7	1.0	1.0	118.7	51.7	170.3
ZnO:Cu (2HEC)	65.2	64.9	1.0	1.0	112.3	39.0	151.3

According to the surface roughness estimation by ImageJ software, the least rough surface belongs to the layer using 2HEC as binder. This is not in compliance with the profile plot measurement. The reason for this

difference could be the lower intensity of fluorescence which could be caused by lower thickness of the film as mentioned above.

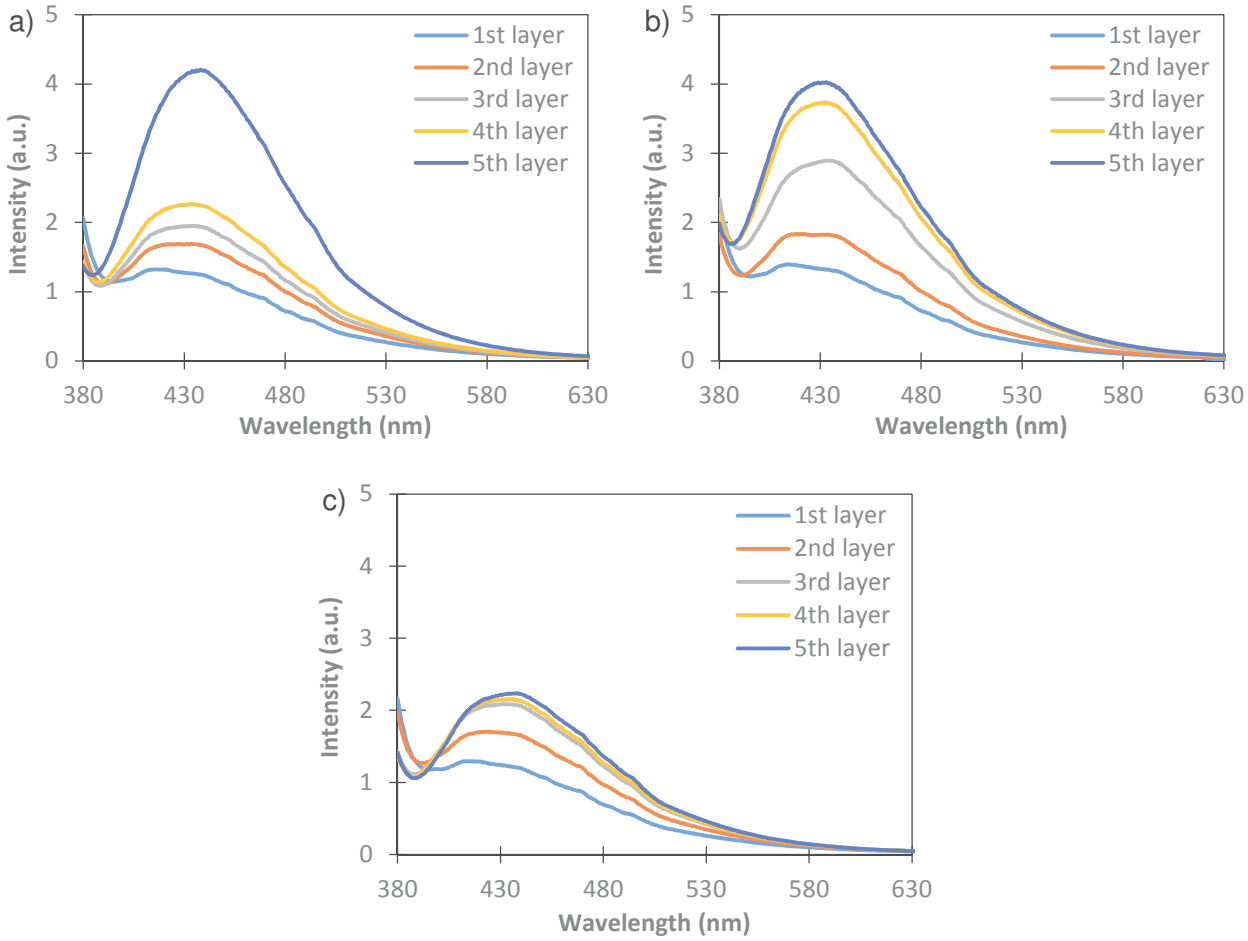

Figure 4 Fluorescence spectra of ZnO:Cu in a) CMC, b) PVP, and c) 2HEC polymeric binders after deposition on Standard IGT paper

The fluorescence of the layers is gaining in intensity differently with each binder. CMC and PVP seem to reach a similar intensity of fluorescence. In case of CMC, gain in intensity of the last deposited layer is much higher than in other cases. Cause of this behaviour will be studied in future research. PVP has a more uniform growth in intensity. In case of 2HEC, it is obvious that the increase of fluorescence after three layers is only in small extent. Thus, more layers are not necessary, because they do not contribute to increase the intensity of fluorescence. These spectra in comparison with those of solutions show similar distributions of intensities. In all cases, the peak is situated at 438 nm. In case of PVP, in the ink composition and up to the second layer, the peak is situated at approx. 414 nm and then changes into a shoulder and the peak at 438 nm becomes dominant.

4. CONCLUSION

We have successfully created printable ink compositions of ZnO:Cu in MEA with three binders, namely sodium carboxymethyl cellulose, polyvinylpyrrolidone, and 2-hydroxyethyl cellulose which were deposited onto Standard IGT paper by screen printing. The best homogeneity of the deposited layers was obtained with CMC, with the overall highest intensity of fluorescence. 2HEC also shows good homogeneity and low roughness of

layers estimated by image analysis. The roughness with CMC and PVP is similar, but the PVP shows poor homogeneity which is caused by formation of clusters in the printed layers.

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