

# Inkjet ink containing inorganic doped semiconductor (ZnS:Mn) nanoparticle pigments

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## ABSTRACT

Inorganic nanophosphors for use in an inkjet ink have been prepared using colloiddally synthesized ZnS:Mn treated with acrylic acid which was polymerized *in situ*. Cubic crystalline ZnS:Mn particles were observed using XRD and SEM. Surfactant, solvent, humectant, and binder polymer were added to assist in assembly into a continuous film, with poly(vinyl alcohol) functioning best as both a viscosity modifier and resin binder. Pigment concentration was optimized at 1 w/w% to achieve jettability and good rheology. This ink was deposited using a piezoelectric Dimatix® inkjet printer to form printed lines of ZnS:Mn-AA and PVA. Photoluminescence (PL) of printed lines on cellulose acetate was qualitatively characterized.

**Keywords:** inkjet, semiconductor, inorganic, phosphor, photoluminescence

## 1 – INTRODUCTION

In the field of printed electronics, a large amount of work has gone into the inkjet printing of both metallic and conjugated polymeric conductive materials [1, 2]. Integration of these materials into larger electronic devices often involves the use of bulk semiconductors and dielectrics. However, of late, semiconductive polymer species and other solution-processed functional materials have attracted attention as alternatives to bulk inorganic semiconductors and dielectrics [3, 4]. Printing of polymers presents difficulties with rheology, droplet formation, and so forth [4]. On the other hand, inorganic ceramic or semiconductor materials that are solution-processed as sol-gels require high annealing temperatures to achieve crystallinity and are therefore often unsuitable for use on flexible polymeric substrates. Earlier studies have demonstrated that by dispersing crystalline semiconductor materials directly into a solvent or preparing them in-situ using colloidal precipitation methods [5, 6, 7], and thereby providing a close degree of control over rheology and

surface tension, inkjettable functional materials could be prepared. These doped semiconductors can be used as luminescent species. They can be applied to a given substrate using simple solution processing methods, with no need for high-temperature annealing.

In this study, semiconductive nanoparticles of ZnS:Mn, a common electroluminescent species, were dispersed and stabilized in both water-based inkjet inks. The inks were made suitable for rheology and particle size restraints imposed by inkjet technology. The effect of loading the ink with polymers as binding matrices was also studied. A film of phosphor ink was tested for photoluminescence in order to qualitatively establish the functionality of the inks. The functional inks have potential use as jettable luminescent species for several types of emissive displays or light sources, while avoiding the use of luminescent conjugated polymers. The narrow emission spectra of inorganic emitters provide more intense light at more tightly controlled frequencies than most polymeric emitters, making them preferable for certain applications.

## 2 – EXPERIMENTAL METHODS

### 2.1 Phosphor synthesis & characterization

ZnS:Mn nanophosphors were prepared in methanolic solution from  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (Sigma-Aldrich,  $\geq 98\%$ , ACS reagent),  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (Aldrich,  $\geq 99\%$ ), and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (Sigma-Aldrich,  $\geq 98\%$ , ACS reagent), using a colloidal method described in reference [8]. The nanophosphors were then treated with acrylic acid (AA) (Sigma-Aldrich, 99%) to increase luminescent intensity [8, 9, 10]. The acrylic acid polymerized during the colloidal reaction and served as both a luminescence enhancer and a capping agent. Sodium lauryl sulphate (SLS) (Sigma-Aldrich,  $\geq 98.5\%$ ) was used as a stabilizer and dispersant for the colloidal particles as suggested in [8]. The ratio of SLS to solids was 1:10. After the reaction was complete, a white suspension of solids was formed in the

solvent; the solids were removed by centrifugation in a Beckmann-Coulter Allegra 25R centrifuge at 4000 RPM for 15 minutes. The resulting precipitate was washed with deionized H<sub>2</sub>O to remove any remaining ions. The dried solid was analyzed for crystallinity using a Philips PANalytical PW1830 x-ray diffractometer (Cu source). A small amount of ink (see following subsection) was jetted on cellulose acetate for EDS analysis in a JEOL JSM-7001F scanning electron microscope.

## 2.2 Preparation of jettable ink

Jettable inks were prepared by dispersing ZnS:Mn-AA nanophosphor powder in water, using ZetaSperser 1200 (Air Products), SLS, and Triton X-100 (Union Carbide, laboratory grade) as stabilizers, glycerol (Sigma-Aldrich, 99%) as a humectant, and poly(vinyl alcohol) (Aldrich, M<sub>w</sub> = 130000, 99%+ hydrolyzed) as a binder to encourage assembly of the particles into a single film. Viscosity was controlled to be in the range of 1-10 cP, surface tension in the range of 20-40 mN/m, and particle size to be below 200 nm to meet specifications for the printer used. Viscosity was measured using a capillary viscometer (Kimax USA, size 100, grade B17) with water as the reference material, at 25 ± 1 °C. Surface tension was characterized using a Wilhemy plate tensiometer (KSV Instruments, Sigma 700, platinum plate) at 25 ± 1 °C. Particle size distribution was found using a laser-Doppler velocimetry zeta-potential analyzer (Beckman-Coulter Delsa 440SX), at 35.2° and 26.3° optical detection angles, 25 ± 0.5 °C, in a quartz cell.

## 2.3 Jetting of ink

One ink containing each surfactant type was jetted from a Dimatix DMP2800 inkjet printer (DMP cartridge, 21.5 μm nozzle diameter, 254 μm nozzle spacing, 16 nozzles). Lines of ink were jetted onto a cellulose acetate substrate at 50°C plate temperature and 23°C cartridge temperature.

## 2.4 PL testing

PL testing was carried out by exposing the printed lines to a UV source at 254 nm wavelength and measuring the emissive spectrum using an OceanOptics USB2000+ spectrophotometer. A printed film of ZnS:Mn-AA-PVA phosphor composite on cellulose acetate was exposed to 254-nm UV.

## 3 – RESULTS & DISCUSSION

### 3.1 Nanophosphor characterization

The crystalline structure of the ZnS:Mn-AA nanoparticles was confirmed using XRD, showing distinct peaks at  $2\theta \approx 30^\circ$ ,  $45^\circ$ , and  $55^\circ$  [11]. These peaks correspond to the Bragg angles ( $28.5^\circ$ ,  $47.5^\circ$ , and  $56.6^\circ$ ) of the lattice planes in the cubic ZnS:Mn structure described by Peng *et al* [12].

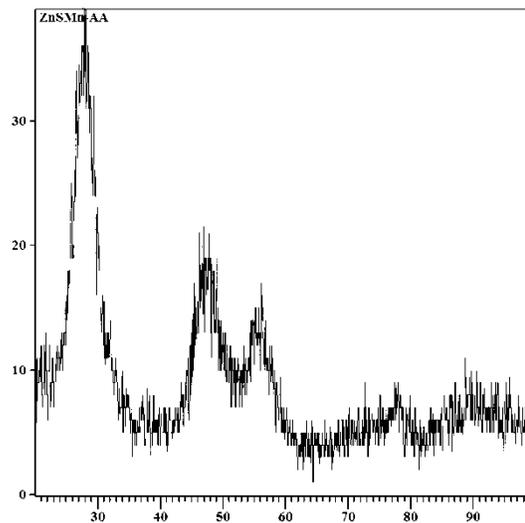


Figure 3.1. XRD spectrum of ZnS:Mn nanocrystals.

SEM imaging confirmed the cubic structure of the crystals, and EDS analysis showed peaks for Zn at both 1 and 8.6 eV, the latter being where its K-line is located. S peaks were more difficult to see due to the presence of large Au and Pd peaks adjacent to them (as a result of the gold coating). However, the tail of the largest Au peak was lengthened by the presence of an S peak.

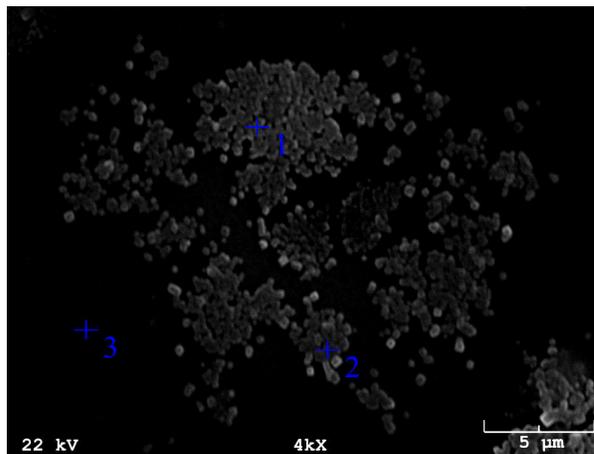


Figure 3.2. SEM image of inkjetted drops. Crosses show points at which EDS analysis was conducted.

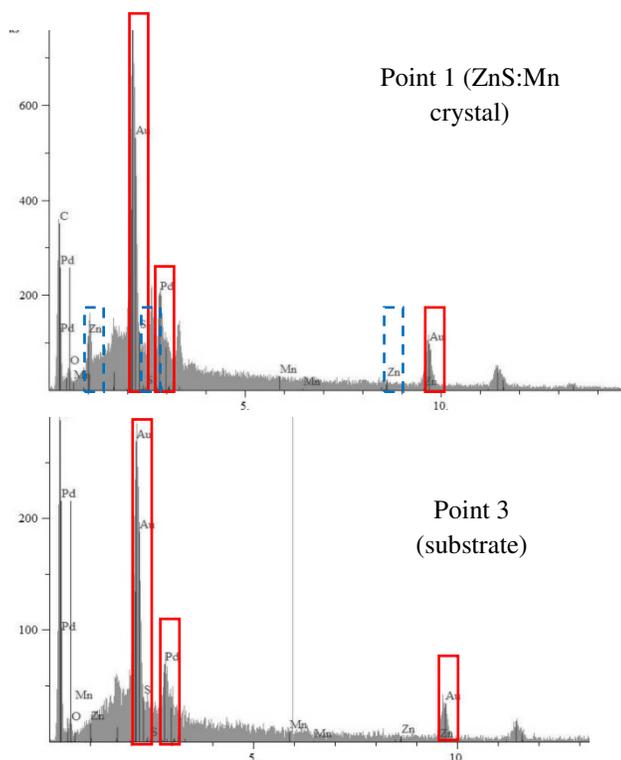


Figure 3.3. EDS spectra taken at points 1 and 3 in Figure 3.2. Red solid boxes show Au and Pd peaks. Blue dashed boxes indicate Zn and S peaks.

Some residual ions such as  $\text{Na}^+$  (from the  $\text{Na}_2\text{S}$  precursor solution) and  $\text{Cl}^-$  (likely from the surfactant molecules) also showed on the spectra.

### 3.2 Ink rheology and jettability

The inks were made according to established inkjet ink proportions in terms of solvent, pigment, surfactant, and humectant loadings. The ink proportions are shown in Table 3.1. These inks contained varying levels of solids, dissolved resins, and solvent. Humectant concentration was held at 20 w/w% (glycerol). All inks contained 0.5 w/w% defoamer (Surfynol<sup>®</sup> DF-110D) as well. Surfactant type was varied for all solid loadings.

Table 3.1. ZnS:Mn-AA-PVA ink formulations.

| Ink  | w/w %   |            |       |         |
|------|---------|------------|-------|---------|
|      | Solvent | Surfactant | Resin | Pigment |
| ZAA1 | 77.846  | 0.1        | 0.554 | 1       |
| ZAA2 | 76.192  | 0.2        | 1.108 | 2       |
| ZAA3 | 74.538  | 0.3        | 1.662 | 3       |
| ZAA4 | 72.885  | 0.4        | 2.215 | 4       |
| ZAA5 | 71.231  | 0.5        | 2.769 | 5       |

Stability of the inks was poor at higher pigment and resin loadings; any inks with higher than 1 w/w% pigment were unstable. These inks would precipitate into agglomerated solids and solvent after only a few minutes. ZAA2 had suitable viscosity for jetting, but the higher concentration of polymers in the solution lead to faster agglomeration. Furthermore, the use of SLS as a stabilizer led to unacceptable agglomeration as well, due to the anionic character of the surfactant and its interaction with the resins in the ink. Triton<sup>®</sup> X-100 caused excessive foaming of the ink, even with higher loadings of Surfynol<sup>®</sup> DF-110D. Therefore, only the ink containing Zetaspere<sup>®</sup> 1200 was jetted. All of the inks containing Zetaspere<sup>®</sup> 1200 had proper surface tension for jetting.

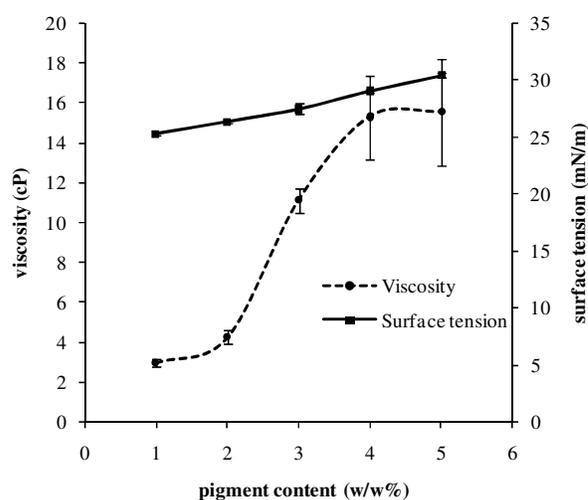


Figure 3.4. Rheology of ZnS:Mn-AA-PVA inks containing Zetaspere<sup>®</sup> 1200, varying solids/resin loadings

SEM imaging (Figure 3.6) showed isolated (not clumped) particle size was approximately 100 nm. Zeta-potential measurements confirmed this particle size (Figure 3.5).

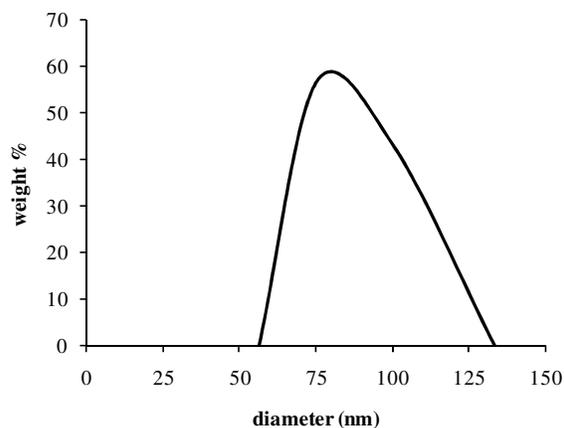


Figure 3.5. Particle size distribution, ZAA1 (Zetaspere<sup>®</sup> 1200 surfactant). Average was  $86 \pm 14$  nm (SD).

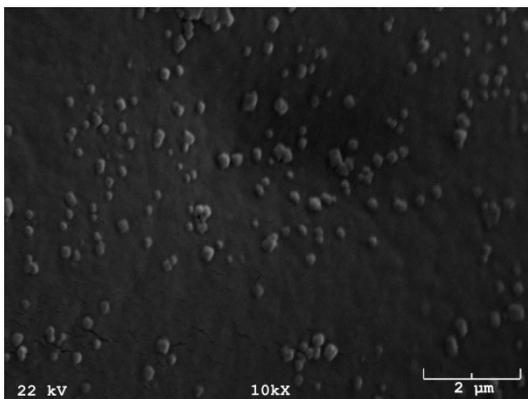
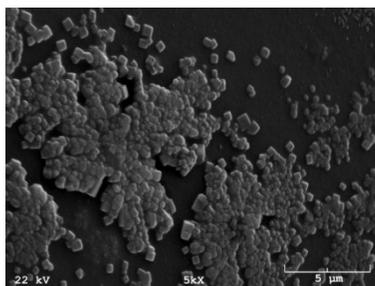


Figure 3.6. ZnS:Mn-AA cubic crystals, inkjetted on cellulose acetate, 10000X

### 3.3 Printed lines

It can be seen in Figures 3.2 and 3.7 that the ink is deposited in small clusters of cubic ZnS:Mn crystals and polymer binder. Between the clusters, continuity in the film is often broken. The size of the small clusters corresponds fairly closely to the predicted size of a jetted drop. Therefore, even though the inks contain sufficient surfactant to allow for stable jetting and wetting of the substrate, they are unable to form continuous thin films. This may also be associated with the polymer content of the ink; between the clumps were scattered isolated particles (Figure 3.6) that had not bonded together into films. However, there is a necessary compromise between jetting performance and polymer content of ink; more dissolved polymer leads to the “bead-on-a-string” effect [1]. In their current form, the films are not sufficiently self-assembled to perform as functional layers in inorganic emissive devices.



3.7a. Two printed droplets of ZAA1 (Zetaspense) ink, 5000X, showing clustering of cubic ZnS:Mn-AA and polymer binder.

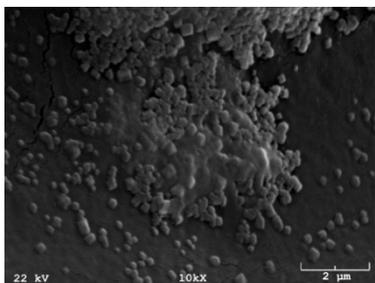


Figure 3.7b. A single printed droplet of ZAA1 (Zetaspense) ink, 10000X showing scattered individual ZnS:Mn crystals on the substrate around the drop.

### 3.4 PL/EL

The discontinuity in the printed lines made them unsuitable for testing for PL or EL. Qualitatively speaking, however, orange emission was visible under UV light where larger clumps of phosphors were clustered. Further work on increasing solids loading and resin loading while maintaining jettability is necessary to address this problem.

## 4 – CONCLUSIONS & FUTURE WORK

It is feasible to stably disperse ZnS:Mn-AA in an inkjet ink and jet it reliably onto a polymeric substrate. However, cohesiveness and continuity of the printed films was compromised by low pigment content and insufficient polymer binder matrix. Balancing the binder and solids contents with the jettability and rheology of the inks presents the major difficult in further developing the ink. Future work will focus on maintaining jettability and improving continuity of the films at higher polymer and solids loadings by careful selection of surfactant and control of particle size during synthesis. We wish to thank the SENTINEL Bioactive Paper Network for their support on this project.

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