Silver Chloride Ink Formulation for Combined Sensor-Antenna Applications

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Abstract

The goal of this research is to formulate silver chloride (AgCl) nanoparticle ink for antenna sensing applications in security printing. AgCl undergoes a chemical decomposition in the presence of ultra violet (UV) light, causing the formation of silver. Proof of concept was performed by ink formulation and conductivity testing of AgCl reduced to Ag. The results of this research suggest that AgCl does not reduce to a continuous, conductive silver path under the conditions studied here.

Introduction

- Counterfeiting methods often involve the manipulation of legitimate packaging materials to repackage counterfeit goods.
- Environmental exposure is common sign tampering has occurred.
- Big Picture: Develop a UV sensitive RF antenna for detecting counterfeiting.
- Primary Research Objective: Develop a UV sensitive ink, composed of AgCl, to act as a UV sensitive switch which activates a RF antenna when exposed to UV light.

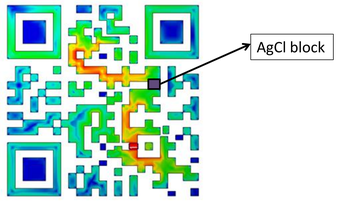

Figure 1. QR Code with AgCl "switch"

AgCl Nanoparticle Synthesis

Procedure 1

- $AgNO_3$ was reacted with HCl in ethylene glycol in the presence of the capping agent PVP.
- Heated to 150^{0}C for 20 minutes. Centrifuged, rinsed with mixture of water and ethanol.
- Produced nanocubes with a mean side length of ~500 nm.
- Room temperature synthesis produced nanocubes with mean side length of ~ 80nm

Procedure 2

- $AgNO_3$ was reacted with NaCl in water with the capping agent PVA.
- Room temperature synthesis for 20 minutes. Centrifuged, rinsed in methanol.
- Nanoparticles produced with mean diameter of ~60nm

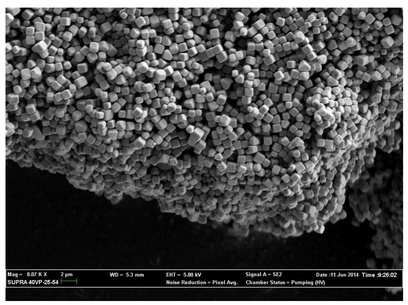

Figure 2. SEM image of 500-nm nanocubes

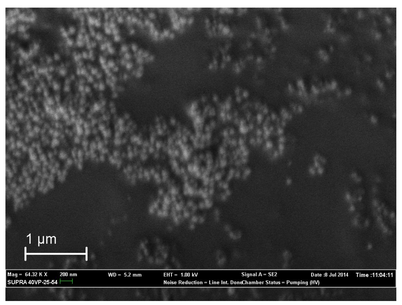

Figure 3. SEM image of 80-nm nanoparticles

Ink Formulation

The Hansen solubility parameters of the 500-nm and 80-nm particles were found by dispersing the nanoparticles in 11 different solvents.

- methyl benzoate, Acetonitrile, diethylene glycol hexyl ether, diethylene glycol, diethylene glycol monobutyl ether, ethylene glycol monobutyl ether, 1-pentanol, ethanol, methanol, ethylene glycol, and water

The 500-nm particles stayed dispersed in 1-pentanol the longest of the solvents, so 1-pentanol was chosen as a solvent for the ink. The 80-nm particles did not disperse in any of the solvents easily, but methanol and water showed more promise. Consequently, a solvent matrix of 70 vol.% methanol and 30 vol.% water was used for the 80-nm particles

Hansen Solubility Parameters

Table 1. Hansen solubility parameters for each synthesis

	δd	δp	δh	R_0	Comments
500 nm	15.98	7.03	12.49	1.9	high yield, low dispersibility
80 nm	13.15	16.04	32.25	11.1	high yield, better dispersion
60 nm	--	--	--	--	low yield, discontinued

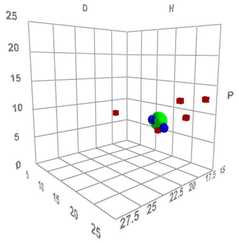

Figure 4. Solubility space for 500-nm particles

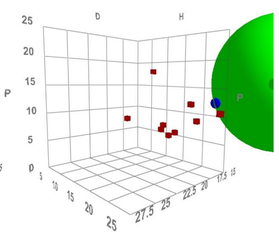

Figure 5. Solubility space for 80-nm particles

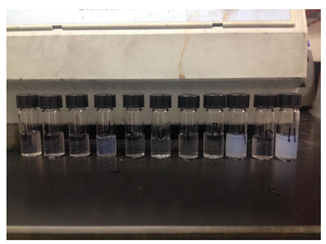

Figure 6. HSP for 80 nm

Spin Coating and Resistance Testing

The 80-nm ink was spin coated on a glass slide at 500 rpm for 1 minute. After which the slide was placed under the four-point probe to measure resistance before and after exposure to UV light.

- Very high resistance before and after exposure to UV light
- Visible color change, but no resistance alteration

Figure 7. Spin coated sample under four-point probe

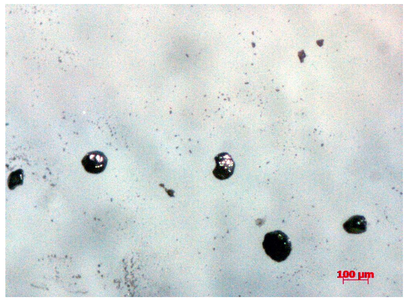

Figure 8. Optical microscope image after exposure to UV

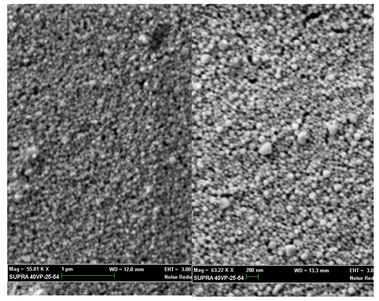

Figure 9 and 10. SEM images of AgCl coated glass slide before and after 1 hour UV light exposure

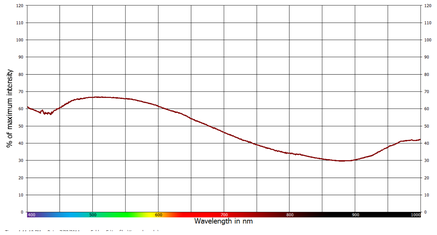

Figure 11. Absorption spectrum suggesting small presence of small silver nanoparticles[1]

Discussion

The relatively large size/tendency to agglomerate of the nanoparticles made determination of the Hansen solubility parameters difficult for both the 500-nm and 80-nm particles.

- 500-nm particles were too large, with the result that settling occurred in approximately 10 min in even the best solvent.
- 80-nm particles tended to agglomerate, with the result that the particles would not stay dispersed in any solution.

The decomposition of AgCl to Ag does not produce a uniform layer of Ag , and therefore does not overcome the percolation threshold necessary to change the resistance.

Conclusions

Neither of the AgCl inks formulated during this research were ideal for the QR code antenna applications. The frequency response of the QR code antenna was designed to change as the result of resistivity changes in the AgCl ink upon exposure to sunlight, but while the AgCl ink does decompose to Ag, this decomposition does not produce a corresponding change in resistance. The AgCl reduces to a non-conductive purple film that may have alternative applications, such as an optically-variable ink, but is not suitable for the QR code antenna application.

Future work for the QR code antenna, the AgCl particles could be mixed with Ag nanoparticles in order to reach the percolation threshold necessary to cause conductivity when exposed to UV light.

References

1. Ankireddy, K., Vunnam, S., Kellar, J., & Cross, W. Highly conductive short chain carboxylic acid encapsulated silver nanoparticle based inks for direct write technology applications. J. Mater. Chem. C, 2013, 1, 572.

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