Printing Upconverting Nanoparticles with a Piezoelectric Inkjet Printer

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Introduction

It has recently become of interest to print upconverting nanoparticles (UCNPs) onto various substrates for security applications. SDSM&T researchers have previously demonstrated the printing of UCNPs using aerosol jet printing methods, shown in Figure 1, printing a quick response (QR) code.

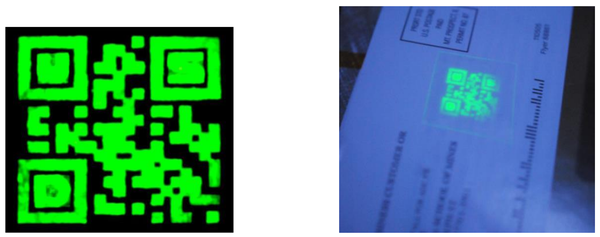

Figure 1: Demonstration of a quick response code printed with upconverting ink using an aerosol jet printer.

This REU Site research involves ink formulations for piezoelectric inkjet printing. To achieve effective printing, initial research focused on formulating an ink with the necessary rheological properties. This included taking both viscosity and surface tension measurements; contact angle measurements were also performed. Two solvents, ethylene glycol (EG) and water, were selected in order to:

1. Achieve a viscosity of 6 – 30 cP; surface tension 30 – 45 mN/m
2. Dissolve polymer additive to form a thin film after printing
3. Disperse the polyacrylic acid-capped UCNPs

The ink should also remain stable over time. If the UCNPs agglomerate or the polymer comes out of solution, printing becomes obstructed. The polymer compositions selected for analysis in these studies included Poly(methyl methacrylate) (PMMA), Polyvinyl alcohol (PVA), and Polyvinylpyrrolidone (PVP) at loadings ranging from 0.1% to 25% weight percent.

Procedure

Ink Rheology

Initial research began with formulaing inks with varying ratios of water to EG for analysis. A Bohlin Instruments viscometer and a Drop Image Advanced imaging equipment/software were utilized. Table 1 shows the results for EG/water ratios. PVA polymer was added with a constant weight fraction of 0.01.

Printing

The piezoelectric printhead is optimal for precise dispensing of printable materials, offering the ability to print four inches across with a single pass. Compared with core classical printing methods, such as screen printing, the Trident 256 Jet printhead provides up to three times higher print resolution. Also, the Trident print assembly is unique in its ability to jet a wide viscosity range from 6 cps - 30 cps. Using an ink in this range is crucial when trying to optimize print resolution.

Results

From Table 1, an EG to water ratio of 4:1 was chosen. Once printing was attempted, however, nozzles became clogged and printing was no longer possible. After re-evaluation of the stability of the ink, it was noticed that high loadings of PVA compared to the ratio of water produced unstable inks, as shown in Figure 2. Table 1 shows the viscosity and surface tension raise and drop, respectively, with the addition of more EG.

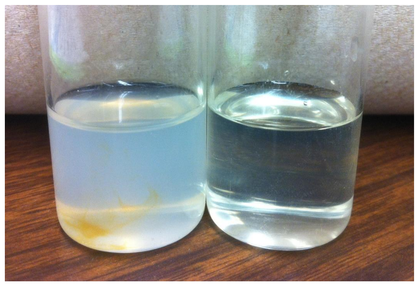

Figure 2: A stable ink on the right compared to an unstable one on the left.

Table 1: Experimental data received from viscosity, surface tension, and contact angle measurements.

Ink containing 1% PVA: varying ratios of water to ethylene glycol M_w(PVA)—31,000 – 50,000 g/mol; ethylene glycol 99% hydrolyzed			
Water : EG	Viscosity (cP)	Surface tension (mN/meter)	Contact angle (steel)
90:10 (%)	1.44	58.9	53.5
85:15 (%)	1.60	57.3	48.8
80:20 (%)	1.70	58.5	41.3
60:40 (%)	3.55	57.5	52.5
50:50 (%)	4.96	57.1	57.2
40:60 (%)	5.74	53.1	54.4
30:70 (%)	7.59	52.3	52.1
20:80 (%)	10.84	49.3	51.0

Discussion

With an ink composition of 20% water, 80% EG, and containing 1 wt% PVA, a rheology near the required values was developed. The surface tension approached the preferred value, although it was slightly higher than desired. The viscosity was in the appropriate range, so preliminarily printing should have been possible. The instability of the ink, however, is expected to have played the key role in hindering performance. To insure a successful print, a known stable ink, consisting of EG and 2-buthoxynethanole with PVP polymer, was analyzed. This ink, had the measured properties show in Table 2.

Table 2: Observed and measured results from stability, surface tension, and viscosity analysis.

Ink containing 0.01 weight fraction PVP: 70% ethylene glycol/30% 2-buthoxyethanole		
Stability	**Surface tension (mN/meter)**	**Viscosity**
Stable	31.50	12.2

Conclusion

Adequate viscosity can be achieved by increasing the ratio of EG to water; surface tension neared the required value was found. However, the solutions were unstable at and below 30% H_2O when using 1.00 wt% PVA. Because the Trident print-head required maintenance, printing analysis could no longer be performed on the inks. In order to insure the use of a working ink, a known printable solution of EG and 2-buthoxynethanole (instead of water), along with PVP polymer, was composed. With sonication, weight loadings up to 1 weight percent UCNPs were successfully dispersed.

References

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