Printing and Patterning of Quantum Dots using Thermal Inkjet Techniques

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Abstract

The merging of traditional non-contact printing methods with recent and rapid advances in the development and synthesis of novel inorganic and organic materials is emerging as an important and versatile research and manufacturing method enabling a wide range of applications. Specifically, the capability to rapidly dispense small, precisely controlled droplets of functional materials with remarkable placement accuracy is accelerating research and discovery in all areas of chemistry, biology, physics and engineering. Furthermore, rapid patterning, accurate drop placement and the sparing usage of costly materials provide an important tool in manufacturing and production. In this paper, we focus on one such application - the use of thermal inkjet printing to deposit and pattern quantum dots. We outline the development and characterization of quantum dot-based inks and discuss the unique challenges that we addressed in fine tuning the ink formulation and chemistry for thermal inkjet deposition. Additionally, we provide an example of how these new quantum dot-based inks and thermal inkjet printing methods can be used to enable new applications.

Introduction

The promises of digital fabrication (DF) and its potential to rapidly advance discovery of applications using nanoscale materials are manifold. On the large scale, expectations are that it can displace lithographic processes, enable roll-to-roll manufacturing, eliminate subtractive processing, and allow real-time processing and modification. On the small or lab scale, DF opens the door to rapid prototyping, judicious use of novel materials that are often in limited supply or prohibitively expensive, desktop fabrication, and reduced waste. One material whose application potential has benefited greatly from DF methods, and indeed may not have been possible without DF, is quantum dots, whose discovery coincided perfectly with the rise in influence of digital desktop printing.[1]

Given the many practical advantages, drop-on-demand printing approaches such as piezoelectric inkjet (PIJ) and thermal inkjet (TIJ) have become the most widely used techniques for digital fabrication applications. Both TIJ and PIJ fabrication techniques have unique advantages and disadvantages and choosing between them is largely based on the properties of the fluid. Since PIJ droplet ejection is based on a mechanically driven impulse, the technique is suitable for the deposition of ink formulations with a wide range of viscosities and solvent-particulate loadings. However, while PIJ offers good fluid latitude, the relatively high costs of the printheads make them less attractive for experimentation, material optimization, and rapid prototyping where disposable printheads are more attractive.

Thermal inkjet (TIJ) printheads are relatively inexpensive yet have not been favored by experimenters for various reasons, only some of which are based in fact. One fact is that the drive bubble strength that enables TIJ ejection is proportional to the heat of vaporization of the fluid, thus limiting solvent latitude to some extent. As a consequence, TIJ is less capable of ejecting viscous fluids. There are two common misconceptions that lead researchers away from TIJ in DP applications. The first is that TIJ is only capable of ejecting aqueous solutions. In fact all liquids which possesses a large heat of vaporization (ΔV) at temperatures below 400 C--water being one of many such fluids—may be a suitable TIJ vehicle. The second is that TIJ heats the ink, implying that temperature sensitive materials cannot survive TIJ ejection. While it is true that a small fraction of the liquid in a TIJ chamber is heated (substantially <1%/volume in most cases), on average the bulk of the ink only sees a temperature increase of 10% above ambient. Thus any material stable at temperatures slightly above ambient may be jetted effectively using TIJ.

In this paper we demonstrate using TIJ for rapid, versatile DF of quantum dots, a highly temperature sensitive material. We discuss creating inks of suitable quantum dots and we give an example of exploiting their narrow emission bandwidth to enable the creation of overt and covert security marks. Ultimately, the narrow emission and absorption bands of printed quantum dots, modulated in intensity or frequency, could be used to create unique, customer-specific security marks offering security that far exceeds what is available today.[2]

Experimental Details and Methods

In order to jet quantum dots with TIJ it was necessary to prepare an ink that demonstrated good jetting properties and kept the quantum dots in suspension. In its simplest guise, a good TIJ ink contains an ejection solvent (typically water) and a colorant (quantum dots in this case). Experience has shown that when water is used as the ejection fluid, a humectant, surfactant, and a buffer are usually required to promote nozzle health, control water evaporation and to keep the colorant in suspension. Generally, we used an alcohol as the humectant, commonly available surfactants, and buffered the inks to a pH of 8-9. In all of our experiments we used aqueous suspensions of CdSe:ZnS and Mn-doped Zn:Se core-shell quantum dots obtained from NN-Labs in Fayetteville, Arkansas. Quantum dot concentration was typically 1-10 mg/ml and the inks were prepared immediately prior to use. Unused ink and filled cartridges were stored in the refrigerator at 4 C.

Images were created using various commercially available Hewlett-Packard DeskJet printers equipped with Hewlett-Packard inkjet cartridges filled in-house with quantum dot inks. The media used was either standard white office paper or Teslin (PPG Industries, Pittsburgh, Pennsylvania). Solution and printed fluorescence measurements were performed on a Photon

Technologies QM-4/2006 spectrofluorimeter. Barcodes were read using an InData Systems (Skaneateles, New York) 3800g handhleld barcode reader equipped with a 380 nm UV LED. A print sample from a typical configuration is shown in Figure 1.

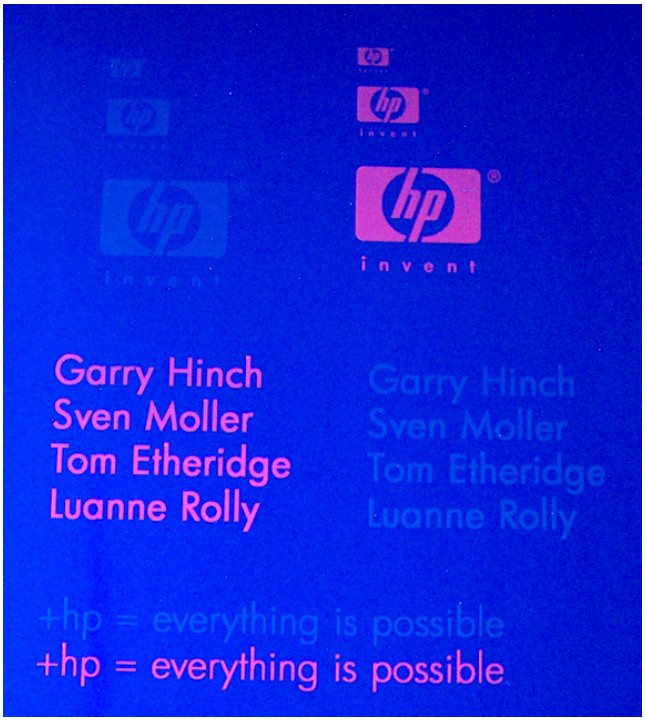

***Figure 1**. Blue- and red-emitting CdSe:ZnS (λ_{ex}=365 nm) core-shell quantum dots printed on plain office paper using a HP95 cartridge running in a HP6540 DeskJet printer. The ink formulation consisted of water, a surfactant and a humectant. The blue background is due to emission from Blankophor P in the paper.*

Observations

Creating jettable inks of quantum dots proved to be relatively simple but creating stable inks – those where the emissive properties of the quantum dots could be observed for days rather than hours – proved to be more challenging. Figure 2 shows the normalized fluorescence of red-emitting CdSe:ZnS core-shell quantum dots in aqueous suspension using four common TIJ humectants as cosolvents. We found that the effective useful life of the ink varied significantly with the humectant used, presumably because some of these humectants displace the ligands from the quantum dots at a greater rate than others, resulting in agglomeration of quantum dots, at a greater rate than others. In no case were we able to extend the useful life of the ink beyond a few days.

The printing system deployed played a minor to insignificant role in image quality or life. This result was not surprising since current consumer TIJ printers are designed to deliver image quality that competes favorably with or exceeds that of silver halide prints. We did note however that quantum dot inks put into cartridges using a foam block rather than a bag as the ink reservoir tended to have a much shorter shelf life. The shorter life may be due to either displacement of the ligands on the quantum dots by the residual surfactants or release agents on the foam, increased oxidation rate of the quantum dots due to adsorption on the foam, or a combination of both.

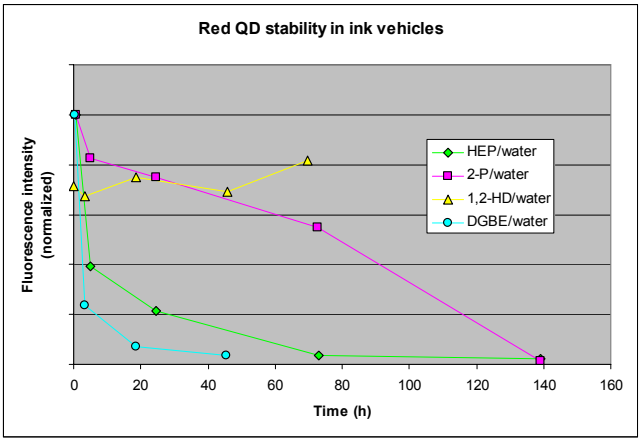

***Figure 2.** Fluorescent life of CdSe:ZnS core-shell quantum dots in aqueous solution with 1-(2-hydroxyethyl)-2-pyrrolidinone (HEP), 2-pyrrolidinone (2-P), 1,2-hexanediol (1,2-HD), or dipropylene glycol butyl ether (DGBE).*

The media itself was found to play a significant role in the overall fluorescent life of the printed image. Images printed on plain paper, whether white office paper or unbleached craft paper, were found to last much longer than those printed on Teslin, a commercial material used extensively for the manufacture of security cards such as driver's licenses and photo IDs. Teslin was of interest for us because it contains no fluorophores, unlike most papers which contain Blankophor P (a fluorescent whitening agent used to make them appear whiter). Even unbleached or untreated papers often contain significant amounts of residual Blankophor P. The images on Teslin were found to fade beyond recognition in a matter of only a few days whereas the images on paper lasted for weeks. Teslin is a silica/high MW polyethylene material and we believe the reduced image life is the result of more rapid oxidation of the quantum dots on the silica surface. In all cases, images printed with CdSe:ZnS quantum dots faded much more rapidly than those printed with Mn-doped ZnSe quantum dots.

A Digital Fabrication Example

We chose to create 2-D barcodes of printed quantum dots as our demonstration vehicle for digital fabrication using TIJ. Barcodes require relatively good resolution in order to preserve their encoded data, are simple to interrogate using handheld readers, can be created and modified readily, and have potential use as security marks. By using quantum dots to create the barcodes we have the potential to embed data spatially, the usual method for black-and-white barcodes, or spectrally, where we exploit the narrow emission bandwidth of the quantum dot fluorescence.

The common CdSe:ZnS core shell quantum dots that emit across the visible spectrum are characterized by a broad absorption band that overlaps the emission band (Figure 3). This absorption makes the printed quantum dot images appear as faint brown squares under ambient lighting making them unsuitable for applications where the barcode would be applied to an

information-rich or branded medium, such as a cereal box or a book jacket. In the Mn-doped ZnSe quantum dots developed by Peng, et al. at the University of Arkansas[3,4] (coined "doped nanocrystals" or "d-dots"), however, the absorption band is displaced well away from the emission band and falls in the ultraviolet region of the spectrum, as shown in Figure 4. This renders the dots and the images created from them invisible under ambient lighting.

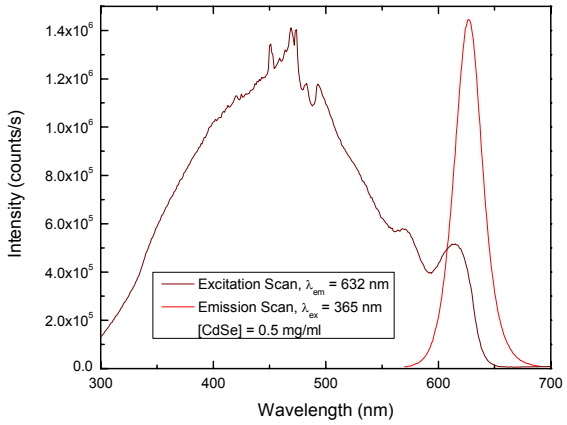

Figure 3. *Absorption (brown) and emission (red) spectra of red-emitting CdSe:ZnS core-shell quantum dots in aqueous solution.*

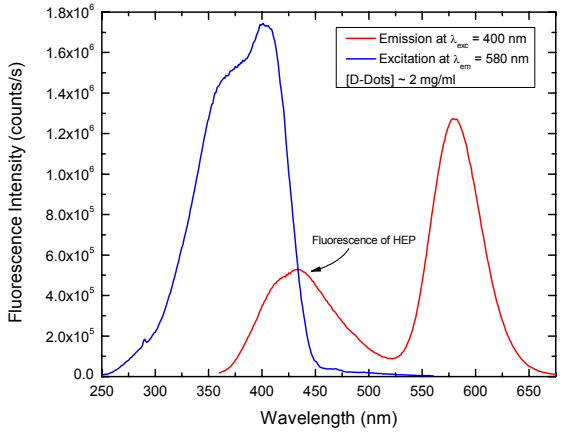

Figure 4. *Absorption (blue) and emission (red) spectra of orange-emitting Mn-doped ZnSe quantum dots in aqueous solution with HEP.*

Using the same ink formulations we developed for CdSe:ZnS core-shell quantum dots we printed 2-D barcodes using d-dots on both plain office paper and Teslin. As expected, these barcodes are invisible under ambient lighting but fluoresce vividly under UV excitation, as shown in Figure 5. The barcodes were easily read by our InData handheld barcode reader at low print density on Teslin and could be read on plain paper if printed in two or more passes (the same result could be obtained with a higher concentration of d-dots in the ink).

Figure 5. *Fluorescent 2-D barcodes printed on Teslin with Mn-doped ZnSe quantum dots (λ_{ex}=365 nm).*

In order to encode data in a spectral format the integrity of the emission band, and most importantly the width of this band, must be maintained in the printed image. We found that the emission maximum did not shift between solution and printed d-dots and the width of the band did not increase (see Figure 6). It should be noted however that the emission bandwidth for d-dots is much wider than it is for most CdSe:ZnS core-shell quantum dots.

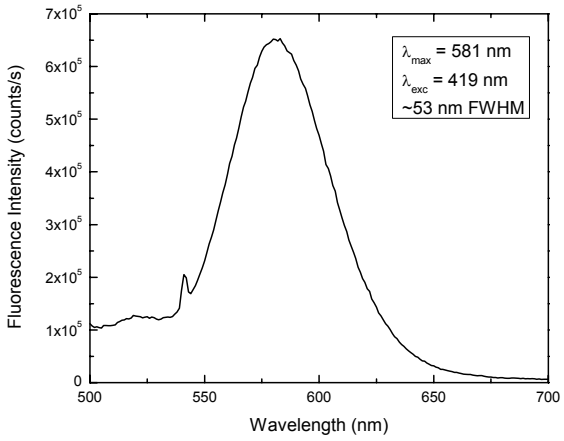

Figure 6. *Emission spectrum of orange-emitting Mn-doped ZnSe quantum dots printed on Teslin.*

Conclusions and Future Challenges

We conclude that TIJ is indeed an effective method for deposition of quantum dots, even those with limited thermal stability. We have created relatively stable, aqueous ink formulations of CdSe:ZnS and Mn-doped ZnSe quantum dots, jetted these inks using off-the-shelf TIJ printers and created text, barcodes and other images on a variety of media using these inks. As a test case we investigated the use of quantum dots for overt

and covert security marks and in so doing have demonstrated that images and patterns can be created that exploit the narrow emission bandwidth of quantum dots whether these materials are mixed in the ink itself or printed adjacently.

The greatest hurdles to future effectiveness and utility of TIJ deposition of quantum dots in DF applications lies not with TIJ technology, but with the quantum dots themselves. For TIJ, or any printing technique, to be useful for any more than prototype applications, more robust ligand spheres—i.e. those with greater pH, temperature, and oxidation stability—must be created. Additionally, quantum dot materials that avoid the use of heavy metals (Pb, Cd, Hg) yet still offer a broad range of emission wavelengths must be discovered. Fortunately, many research labs are vigorously tackling these issues and the future of digital fabrication with quantum dots is bright.

Incremental developments in TIJ will also enable DF. Greater solvent flexibility would permit greater flexibility in molecules used for quantum dot ligands and may provide greater ink stability by reducing the likelihood of agglomeration. Other solvents may also , enhance the ink/media interaction (expanding the potential application space), and may improve the shelf life of the ink.

References

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Author Biography

Tom Etheridge received his BS in chemistry from the University of West Florida (1988) and his PhD in chemistry from the University of Chicago (1993). He has worked in various aspects of thermal inkjet printing at Hewlett-Packard since 1994. Most recently his research has focused on extending thermal inkjet printing into non-traditional areas, such as creation of photonic crystals and printing of nanoscale materials. He is a member of ACS, MRS and Sigma Xi.