Drop-on-Demand Ink-jet printing of Functional Materials: Case Studies of SU8 and NC based Polymer Nanocomposites

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Abstract

Ink-jet printing technique allows locally and precisely dispensing of materials for the manufacturing of micro-scale structures. We present two different applications: i) fabrication of convex microlenses using SU-8 a photo-curable epoxy-based polymer and ii) printing of color pixel arrays using differently sized CdSe@ZnS core-shell type nanocrystals (NCs) embedded in polystyrene. Patterns of such materials are printed on different substrates. We investigated the influence of the surface conditions on the size and shape of the printed patterns, which is affected by wetting properties. The size dependent optical properties of the NC based nanocomposite inks have been demonstrated to be retained in the printed structures.

I. Introduction

An ink-jet printing process has been developed, which allows the design and flexible direct and mask-free fabrication of structures on various substrates. The main asset of ink-jet printing technology is that the functional material can be printed where desired and no developing steps are required. This technique is very simple when the ink-jet printing parameters are optimized, and flexible when compared to photolithography [1]. Moreover, this is a cost-effective process when expensive commercial or custom designed inks are used. The drop-on demand (DOD) mode is a method where single drops are generated and printed at the desired position and time with high accuracy and with reduced material waste [2, 3]. Furthermore the alignment of the nozzle to pre-structured substrates is feasible in this mode.

In this paper the DOD ink-jet process is used for two applications: i) fabrication of microlens arrays using SU-8 in gamma-butyrolactone (GBL), ii) printing of single-/multi-color pixel arrays by using different diameter CdSe@ZnS nanocrystals (NCs) incorporated in chloroform solutions of polystyrene [4]. Colloidal semiconductor NCs were here incorporated in the host polystyrene matrix in order to achieve original nanocomposite where to effectively convey their size depending absorption and emission properties. The ink-jet printing parameters were optimized in order to generate stable and reproducible drops for each material in both continuous and DOD modes. Finally, we fabricated arbitrary patterns of (i) convex microlens arrays and (ii) single-/multi-color pixel arrays onto surface-functionalized substrates and onto glass substrates. We also investigated the influence of the surface conditions on the size and shape of the printed patterns, which can be affected by wetting properties. Further characterization and results will be presented in the paper.

II. Experimental Techniques

Ink-jet printing devices

Ink-jet printing was performed by using a piezo-actuated ink-jet printer purchased from Microdrop Technologies. The nozzle is actuated in squeeze mode. The generation of drops was observed with a stroboscopic system when tuning the signal amplitude and pulse length of the piezo-actuator. The pressure in the reservoir was controlled to optimize the liquid flow, the wetting of the nozzle and ejection properties. The substrate was positioned relatively to the print nozzle with a motorized high-precision X-Y-θ stage (Figure1). Different nozzles having a diameter in the range of 50 to 100 μm were used to print microlens and color pixel arrays of single- or multi-microdrops.

Ink-jet printing of SU-8

We use a piezo-actuated inkjet printer head with a nozzle aperture of 50 μm with a heated nozzle to fabricate microlenses using SU-8 (provided by micro resist technology, Germany). The drops are observed by a stroboscopic vision system. Patterns made of single drop of SU-8 are created either in continuous or DOD mode. In the continuous mode the shape of the final pattern is determined by the frequency of generating drops, the scan speed of a motorized stage, and the dwell time of the printed microdrops.. The DOD mode enables the deposition of microdrops individually at due times and positions. After deposition, the drops are prebaked (100 °C for 15 minutes), UV-exposed (400 mJ/cm^2) and post-baked (100 °C for 15 minutes).

Ink-jet printing of polymer nanocomposites

The ink-jet printer head with 70 μm nozzle diamter was used to print color pixel arrays. Polystyrene (PS) based nanocomposites that contain highly luminescent CdSe@ZnS NCs in a single solvent, $CHCl_3$, have been chosen as inks [4].

Colloidal NCs can be properly tailored in order to tune their opto-electronic properties as function of size. Here highly emitting organic soluble CdSe@ZnS NCs, in size ranging from 2.7 to 4.6 nm, coated by organic surfactant molecules and soluble in organic solvents have been synthesized by slightly modifying the procedures reported by Mews et al [5] and were embedded in the organic host matrix in order to convey their size dependent emission into the PS based inks. PS is selected for its attractive properties, such as high flexibility, good processing capability, high optical transparency.

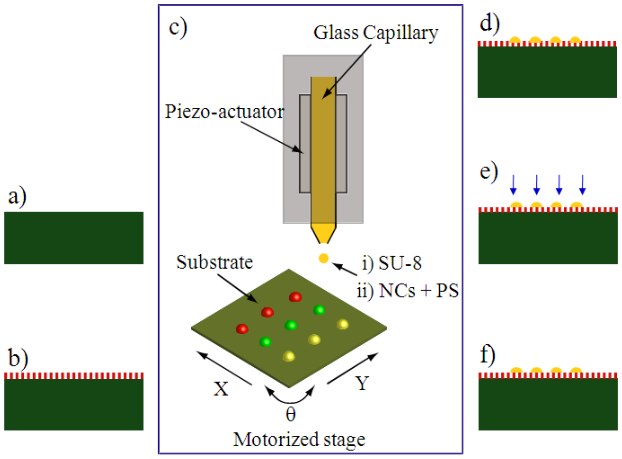

***Figure 1**. Schematic illustration of the experimental procedure: a) substrate preparation, b). surface treatment (e.g. SAM treatment, coating …), c) Inkjet printing: a glass capillary is actuated in squeeze mode by a piezo-actuator. A pressure wave is generated which leads to the generation of micro-drops., d) Pre-bake, e) UV-exposure, f) post exposure bake*

Characterization Techniques

The deposited micro-structures were observed using an optical microscope. A Scanning Electron Microscope (SEM) and an optical profiler are used to inspect the 3D shape of the printed microlenses and color pixel arrays which are coated by a 30 nm-thick layer of gold to reduce charging. Fluorescence optical images have been recorded by means of a Carl Zeiss Axio Vision Product Suite CD25 equipped with an AxioCam MRc 5, irradiating the samples with light filters.

For microlens characterization two different characterization methods based on a He-Ne laser and a Mach-Zehnder interferometer were used to determine the focal distance/length and the numerical aperture.

III. Results

Microlenses fabricated by inkjetted SU-8

We fixed the inkjet parameters experimentally [6] in order to obtain stable drops, without any satellite-drop generation.

The shape and diameter of microlenses can be affected by the surface wetting properties. The mean value of the diameter of single microlenses fabricated using SU-8 was measured and is shown in Figure 2. The mean diameter *d* was reduced from 117 µm for non-treated silicon to 58 µm for a silicon wafer coated with a self-assembled monolayer (SAM). Therefore, as expected, the contact angle and the size largely depend on the substrate for the same amount of material.

The 3D shape of the microlenses has been investigated by tilted SEM imaging. As anticipated and shown in Figure 3, a significant increase in microlens height occurred in the case of the substrates coated with the SAM layer. We have evaluated the optical properties of the microlenses using a Mach-Zehnder interferometer. The focal length (*f*) and NA are summarized in table 1. Both *f* and NA can be tuned readily by varying for instance the number of drops from one to two per microlens.

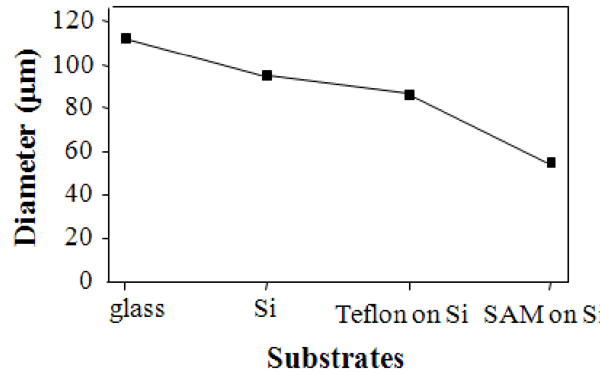

***Figure 2**. Mean diameter of the ink-jet printed microlens on various surface treated substrate.*

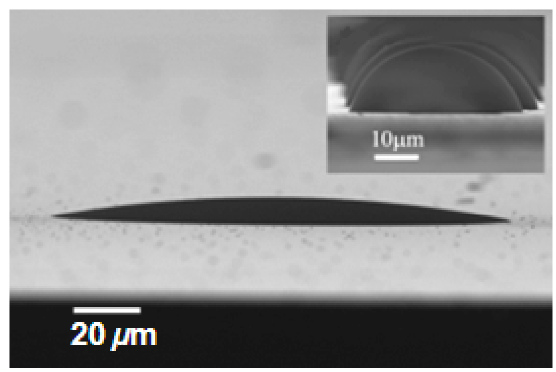

***Figure 3**. SEM image of a typical ink-jet printed microlens having a diameter of 117 µm on silicon substrate. In the inset figure, a SEM image of the ink-jet printed microlenses is shown in which the diameter is reduced to 58 µm on SAM-coated silicon substrate.*

Table 1. Optical characteristics of ink-jet printed microlenses using SU-8 on SAM-coated glass substrate.

#. of drops/microlens	f (µm)	NA
Single drop	42	0.46
Double drops	73	0.25

Color pixel arrays of CdSe@ZnS nanocrystals in polystyrene based nanocomposites

CdSe@ZnS NCs having three different sizes, 2.7, 3.4 and 4.6 nm, respectively, characterized by green, orange and red size dependent emission, have been incorporated in PS based solution to generate multicolour patterns (See figure 4). PS solution in

$CHCl_3$ in a range of concentration from 1 to 5 wt% were ink-jet printed both in continuous and in drop-on-demand modes (DOD) by using 70 µm in diameter of the nozzle. The stability and the reproducibility of the drops in $CHCl_3$ have been monitored by a stroboscopic system, and stable drops were obtained for PC concentrations above 3 wt%.

Therefore the two PS concentration values of 3 and 5 wt% are selected for further investigations in $CHCl_3$ to compare their optical and morphological behavior.

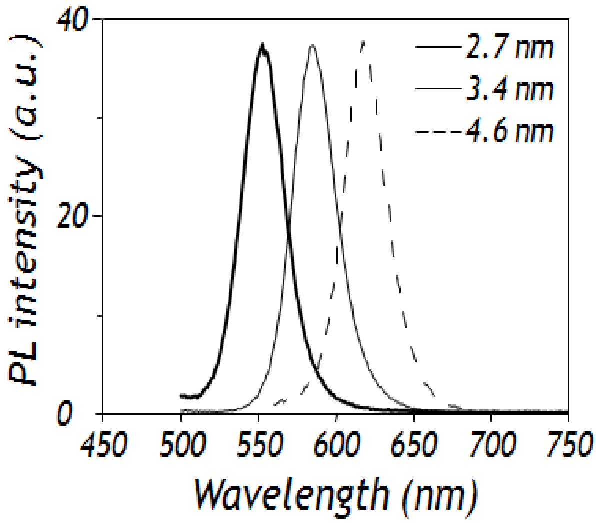

***Figure 4**. Photoluminescence (PL) spectra of 2.7, 3.4, and 4.6 nm diameter CdSe@ZnS NCs in $CHCl_3$ at the excitation wavelength (λ_{exc}) of 400 nm.*

The molecular weight and the concentration of the polymeric composite play an important role in determining the filament formation during the inkjet printing process [1, 7-9] on which depends the stability of the generated drops. The length of the filaments increase with the molecular weight and concentration of the polymer leading to the generation of satellite drops responsible of the instability of generation. Such long filaments have not been observed in the case of PS solutions with concentrations ranging from 3 wt% to 5 wt% at a molecular weight of 5000. Therefore stable drops have been generated.

Images of ink-jet printed pixels are shown in Figure 5 (a) and (b) Figure 5 (a) shows pixels, obtained by depositing 25 drops per pixel, having regular shape without any satellite beside of main printed pixels. The optimal number of droplet per pixel has been found out upon checking the shape and reproducibility of the printing process. In Figure 5 (b), slightly dark area in the central region of the droplets can be observed. Interestingly no significant “coffee-stain” effect seems to affect the printed pixels, in spite of the fact that a single-solvent ink has been used. At the increasing of evaporation time the droplets profile evolves, resulting typically thinner in the centre than at the edges and generating a “concave-disk” shape caused by a non-uniform speed of solvent evaporation which in fact decreases passing from the centre of the droplet to the edges.

Using these optimized nozzle settings pixels of 25 and 50 drops of CdSe@ZnS NC nanocomposites based on 5 wt% of PS have been ink-jet printed in single- and multi-color arrays. The fluorescence optical microscope images of single- and multi-color arrays (≈ 27 x 27) are shown in Figure 6. This photograph is taken by a conventional digital camera in dark area under UV illumination. Such multi-color arrays were sequentially ink-jet printed by depositing with a single-nozzle system 25 drops per pixel of differently sized CdSe@ZnS NCs embedded in PS (5wt%) based nanocomposites. The inset image in Figure 6 is also fluorescence images of single-color arrays (9 x 9) ink-jet printed with 2.7, 3.4, and 4.6 nm sized CdSe@ZnS NCs embedded 5 wt% PS nanocomposites corresponding to green, orange and red, respectively.

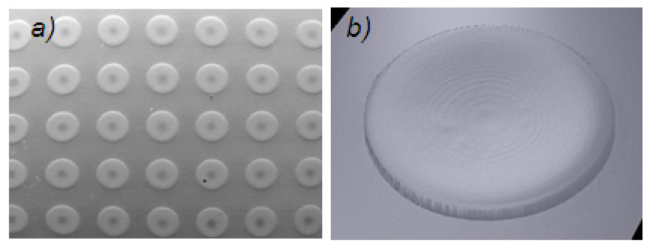

***Figure 5**. a) SEM and b) optical profiler images of 25 drops based pixels ink-jet printed using 3.4 nm sized NCs embedded 5 wt% PS nanocomposite in $CHCl_3$.*

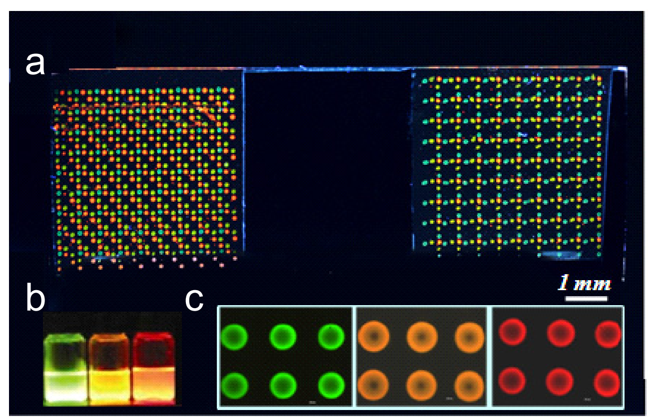

***Figure 6**. (a) Fluorescent photograph of inkjet-printed multi-color pixels (27 x 27) by UV lamp λ_{exc} 366 nm, formed by 25 drops obtained by using inks based on CdSe@ZnS NCs of different sizes (2.7, 3.4, and 4.6 nm, respectively) dispersed in 5 wt% PS (b). In the panel (c) fluorescence optical microscopy images, of single-color arrays of the same ink-jet printed NC based nanocomposites (5 wt% PS). Each pixels's size is ~ 600 µm.*

IV. Conclusion

Inkjet printing technology has been here proven to direct patterning polymer based materials, namely SU-8 and luminescent NC based PS nanocomposites. The parameters for properly inkjet printing each investigated material have been defined through an accurate screening of the optimal conditions.

SU-8 microlenses have been ink-jet printed on different surfaces having different diameters on various surface conditions. The diameter changes of the microlenses from 117 µm to 57 µm. Our results show that directly inkjet printed SU-8 microlenses show promising characteristics for micro-optical applications.

CdSe@ZnS NC based PS nanocomposites have been used as inks. In particular the size dependent luminescence of the colloidal CdSe@ZnS NCs has been exploited in order to obtain differently emitting nanocomposites simply tuning the size of the inorganic counterpart embedded in the PS, thus achieving green, orange, and red emission colors, respectively. The obtained inks were ink-jet printed with optimized ink-jet parameters with the most stable and reproducible droplets. In this work, a single solvent system, $CHCl_3$, demonstrated the possibility of using a relatively low-boiling temperature solvent for ink-jet, preserving a good printability, without significant "coffee stain" effects. Despite the fact that the dried droplets show a slight concavity, highly reproducible single- and multi-color arrays have been ink-jet printed in green, orange and red on glass substrates. We also fabricated 27 x 27 multi-color arrays by combining the 3 different colours with very precise positioning.

Further studies will include the extensive optical and morphological characterization of the obtained structures, in order to further address the fabrication of devices for technological applications such as light emitting devices.

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VI. References

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Authors Biographies

Joo Yeon KIM received her Ph.D. in material science and engineering from the Hannam University in 2006. She then worked at Korean Institute of Materials and Machinery (KIMM) as a research fellow to improve the hydro-philic/phobic properties of the materials for UV nanoimprinting lithography (UV-NIL). In 2007, she joined Prof. Juergen Brugger's group at Ecole Polytechnique Fédérale de Lausanne (EPFL) as a post-doctoral research fellow with her interests in ink-jet printing for micro-/opto-electronic applications with electrical/optical grade polymers and polymer nanocomposites.

C. Ingrosso was born in Lecce (Italy) in 1980. She got her degree in Chemistry in 2004 from the University of Bari (Italy). In 2007 she obtained her PhD in Chemistry from the same university, with a thesis in the preparation and characterization of hybrid organic/inorganic materials based on colloidal nanocrystals towards sensing applications. At present, she has a position as Post Doc under the supervision of Prof. A. Agostiano of University of Bari and works in constant collaboration with CNR-IPCF Bari Division Nanochemistry laboratory. Her assets relay on the synthesis and characterization of colloidal semiconductor and magnetic nanocrystals, their incorporation in polymers and organization onto functional polymer based surface responsive microcomponents for the development of novel nanocomposite materials and probes with new properties appealing for advanced MEMS/NEMS device sensing and optoelectronic applications.

Marinella Striccoli obtained her degree in Physics in 1992 at University of Bari (Italy). In 1995 she was visiting scientist at the AT&T Bell Labs under the supervision of F. Capasso. From 1992 to 2000 she worked as researcher at Centro Laser research center, then for 2001 she had a grant fellowship from INFM. Since 2002 she has joined CNR (Italian National Research Council) as staff researcher in the Institute for Chemical Physical Processes. She has been responsible and involved in several National and European Projects in the field of Material Science and semiconductor nanostructures. Now her research interests are mainly focussed on colloidal nanocrystals structures (semiconductors, metal and oxide), in their organization in ordinate assemblies and in the development of nanocomposite materials. She is co-author on more than 30 papers on international peer reviewed journals and several conference contributions.

M. Lucia Curri obtained her Chemistry degree in 1992 at University of Bari (Italy). In 1997 she got her PhD in Chemistry from the same university, with a thesis in archaeological chemistry. She had then a research assignment at University College of London (UK) and then joined CNR (Italian National Research Council) with a grant fellowship in 1997 and is working as staff researcher since 1999. She is the scientific responsible of several National and European Research Projects in nanomaterial chemistry. Her research interests include development of chemical methods to prepare nanoparticles of semiconductors metal and oxides and to organize them in mesostructures, or incorporate them in polymers for developing novel nanocomposite materials and 2/3 D nanoparticle assemblies. She has co-authored more than 60 papers on international journals

V. Fakhfouri received a EPFL Engineering Diploma (Master) in Microengineering with a specialization in Robotics and Assembling Systems. He is now working towards his Ph.D. in the field of "Inkjet printing and Micromolding for the microfabrication of doped and modified polymers".

Juergen Brugger received a Dr.sc. degree from the University of Neuchatel in Physical-Electronics. He is currently Associate Professor in Microtechnique at the Ecole Polytechnique Federale de Lausanne (EPFL) since 2001. Since 1995, he works in the field of interdisciplinary and experimental micro and nanotechnologies towards integrated micro/nanosystems with components at mesoscopic scales. In his research, he combines methods of clean-room technologies with emerging micro and nanopatterning methods, such as scanning probes, stencil lithography and inkjet printing, to be applied to the field of information technologies and life-sciences. Dr. Brugger has published over 80 peer-reviewed scientific publications. He serves as editorial board member of the IOP journal "Nanotechnology" and is nominated General Chair for the Eurosensors XXIII, Lausanne, 2009.