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Micro-Reactive Inkjet Printing of Polyaniline

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Abstract

Inkjet printing, the digitally-controlled deposition of microdroplets onto a substrate, presents a number of potential advantages as a polymer additive manufacturing technique due to a relatively high spatial resolution and the ability to easily deposit multiple materials in one structure. It is, however, fundamentally limited by the low viscosity of the printed ink, which limits both the amount of solid phase present within the ink or necessitates the use of post-deposition curing of the ink to form the structure. Micro-reactive inkjet printing attempts to circumvent these limitations by exploiting the controlled in-air collision of two complementary reactive microdroplets, so as produce a microdroplet of the desired product before impact with the substrate. In this work, we explored the formation of polyaniline (PAni) on glass substrate through oxidative polymerisation of aniline in an acidic environment via a micro-reactive inkjet printing technique. We successfully printed different patterns of polyaniline onto glass substrates, as shown by microscopy and spectroscopy, and a conductivity of approximately 0.6 S cm-1 was achieved. We envision this printing technique to be particularly useful for a wide range of conducting polymer synthesis in the future.

Introduction

Reactive inkjet printing, also known as sequential printing has emerged as a powerful tool enabling the production of patterned and localised functional materials by synthesising and printing of two different materials on the substrate[1]. However, this technique exhibit issues (e.g. only applicable for non-volatile materials, precise control of humidity and inaccurate positioning [1]) that must be resolved before they can be applied to a wider variety of functional materials.

Binary droplet collision is a phenomenon where two droplets of identical or non-identical size droplets collide and/or combine, and has previously been investigated in relation to the formation of raindrops, and fuel combustion [2], [3]. Numerous experimental studies focussed on the relationship between collision outcomes to a geometric impact parameter and Weber number [2],[3]. Subsequently, five distinct patterns of binary droplet interactions have been distinguished, specifically, (I) coalescence after minor deformation, (II) bouncing, (III) coalescence after major deformation, (IV) reflexive separation and (V) stretching separation [2]. Most of this research has used the same liquid for both droplets in the collision, such as hydrocarbons [2], water [4], oil [5], ethanol [6] and only a few with two different liquids [7]. Recently, Hinterbicher et al. suggested that the coalescence of binary or ternary droplet systems of different reactive materials has unprecedented advantages in the formation of transient micro-reaction vessels for chemical synthesis [8]. Hence, inkjet printing and mid-air coalescence of two or more reactive materials may provide new functionality and insights into micro reaction of patterned functional materials.

Intrinsically conducting polymers are considered excellent candidates for flexible electronics due to their mechanical flexibility, light weight, solution processability and comparatively lsow cost [9]. Unlike conventional semiconductor materials that are rigid and bulky, conducting polymers have great potential applications in next-generation electronic devices that requires printability and flexibility. Polyaniline (PAni), prepared by the oxidation of aniline salt is one of the most studied conducting polymers, along with polypyrrole and poly (3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). Several methods have been previously used to fabricate polyaniline including spin coating and spray coating, however, the fabrication mechanism limited the possibility of high resolution and customisation of printable features.

Numerous methods have been employed in the inkjet printing of polyaniline. For example: I) a silver nitrate solution onto substrates previously soaked in aniline monomer and exposing them under UV light [10], II) an aqueous PAni nanodispersion doped with dodecylbenzenesulfonic acid (DBSA) [11], III) a water-dispersible PAni-poly(4-styrenesulfonate) (PSS) nanoparticulate [12], IV) an oxidant solution of ammonium persulphate (APS) and exposing it to aniline monomer and dilute hydrochloric acid vapour [13] and V) sequential printing of solution containing oxidant and solution containing aniline and phytic acid [14].

Here we develop a new technique called micro-reactive inkjet printing, for single step synthesis and deposition of functional materials as shown in Figure 1. The functional materials can be synthesised by collision and coalescence of two reactive microdroplets, so as to produce a microdroplet of the desired product before deposition onto the substrate. As a result, this technique eliminates the evaporation, positioning and limitations on particle size that can otherwise occur in inkjet printing.

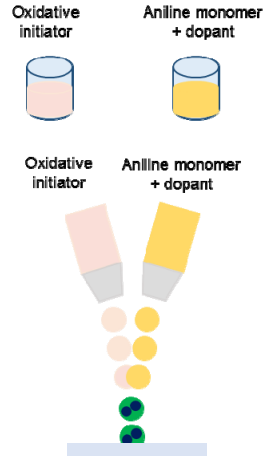

***Figure 1**. Micro-reactive inkjet printing of PAni.*

In this contribution, we present our custom-made micro-reactive inkjet printer, which is able to eject two different reactive droplets and coalesce in mid-air to form the desired product. A microscope camera is installed to monitor the droplet collision and coalescence. We demonstrate our technique by synthesising PAni with droplets containing the oxidative initiator and droplets containing the aniline monomer

on a glass substrate. A series of electrical, chemical, structural and optical properties of this micro-reactive inkjet printed polyaniline will be presented.

Experimental Section

Materials and preparation. Solution A containing 0.4 g ammonium persulfate (APS), 0.2 g ethylene glycol (viscosity modifier) were vigorously mixed in 2 g deionised (DI) water. In addition, 1 wt % of Triton X-100 was added to the Solution A. Solution B comprising of 0.46 g aniline and 0.92 g phytic acid (50%, wt/wt in water) were dissolved in 2 g DI water. Both solutions were filtered through 0.45 µm filter to remove large particles. All chemicals were purchased from Sigma-Aldrich and used as received.

Micro-reactive Inkjet Printer. The inkjet dispensing setup mainly consists of drive electronics (JetDrive III CT-MC3-4, Microfab Technologies, Plano, TX, USA), pressure controller (CT-PT-4, Microfab Technologies), two printheads (MJ-ATP-01, 60µm diameter, Microfab Technologies), LED and USB microscope. Also, mechanical mountings were used to mount various components (LED, camera and printheads) and align them with respect to each other. Lastly, a high resolution 2D motorised stage (Suruga Seiki PG650-L05AG-E1) is positioned underneath the dispensing setup for patterning. More details about the micro-reactive inkjet printer have been published in our earlier paper.[15]

Synthesis of Polyaniline by Micro-reactive Inkjet Printing. Both the Solution A and Solution B were loaded into separate printhead reservoirs. Droplets are ejected from both nozzles and coalesce in mid-air to initialize the synthesis reaction before reaching the glass substrate. Unless stated otherwise, all the samples were inkjet printed onto 10 mm x 10 mm glass substrates that had been cleaned with a detergent solution: sonicated in acetone and isopropyl alcohol for 10 min each.

Characterisation of the Polyanilines films. The sheet resistance of the films were measured by four-point-probe method (N=6). The current and voltage were applied and measured using 4-wire sensing Keysight B2902A. Film thickness was determined using a Bruker Dektak XT. FTIR measurements were done on a NICOLET iS50 FT-IR. UV-vis spectra was recorded on a Perkin-Elmer LS 55. SEM image was taken with a JEOL-JCM 6000. TEM image was acquired with a Technai 12 microscope operated at 120 kV. AFM images were taken in tapping mode using a MFP-3D Origin AFM. XRD pattern was obtained using a ULTIMA IV Rigaku in a conventional θ/2θ geometry.

Result and Discussions

The micro-reactive inkjet printer, consisting of waveform control system, fluidic system, observation system, printing system and motion control system is shown in Figure 2.

Solution A containing ammonium persulfate is loaded into the first reservoir and solution B containing aniline and phytic acid is loaded into the second reservoir. Two droplet coalescence was observed and recorded using a USB microscope as shown in Figure 3. Both droplets are ejected from their respective printhead nozzles and travel at a speed of approximately 3.5 m s^{-1} and form a single droplet travelling at around 3 m s^{-1} in the vertical plane upon coalescence. The entire binary droplet ejection, collision and coalescence takes approximately 1 millisecond.

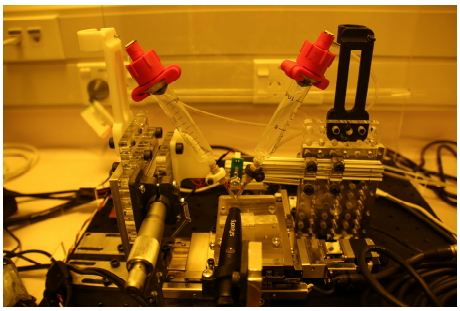

***Figure 2**. Micro-reactive inkjet printer.*

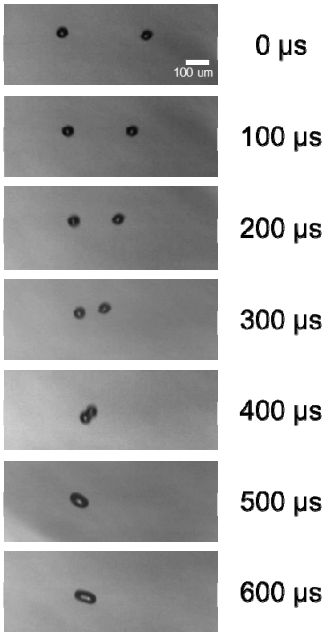

***Figure 3**. Photographic images of coalescence of APS and aniline/Phytic acid.*

Various 2D micro-reactive inkjet printed polyaniline patterns on a glass substrate are shown in Figure 4. A solid thin film of 6 mm x 6 mm square, ~2 µm thick (Figure 4a), a square of 4 mm x 4 mm (Figure 4b) and a triangle of 3 mm x 4 mm (Figure 4c).

The electrical properties of micro-reactive inkjet printed polyaniline thin films were investigated. The conductivity achieved is approximately 0.6 S cm^{-1}, in comparison to the highest conductivity of inkjet printed polyaniline in the literature previously of 0.05 S cm^{-1}.[16] This value of conductivity is significantly greater than previously reported for inkjet printed PAni, and we hypothesise that this is due to the in situ formation of interconnected PAni domains in the reactive process, rather than relying on percolation of individual PAni nanostructures for the conductive network.

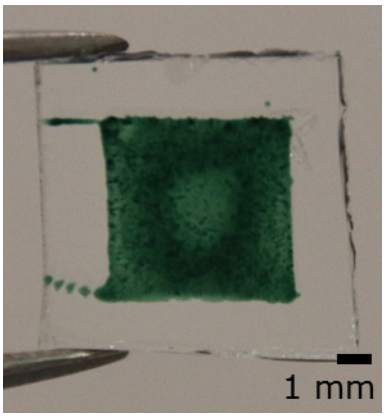

Figure 4a. *PAni thin film on glass substrate.*

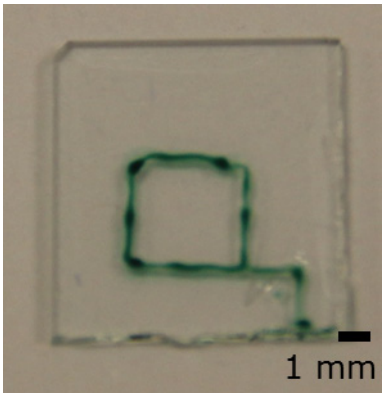

Figure 4b*. Square PAni on glass substrate.*

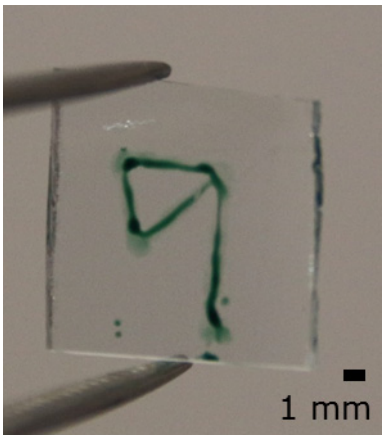

Figure 4c. *Triangle PAni on glass substrate.*

We performed Fourier transform infrared (FTIR) measurements on the micro-reactive inkjet printed PAni film as shown in Figure 5. The FTIR spectra clearly show that there is an emeraldine salt form of Pani with two peaks situated at 1574 cm^{-1} and 1492 cm^{-1} arising from the stretching vibration of quinoid and benzenoid ring, respectively.[17] The absorption around 1301 cm^{-1} and 1246 cm^{-1} is attributed to the C-N stretching vibration for aromatic conjugation.[18] Other peaks 1124 cm^{-1}, 896 cm^{-1} and 800 cm^{-1} can be assigned to the bending vibrations of the C-H bonds on aromatic rings.[18]

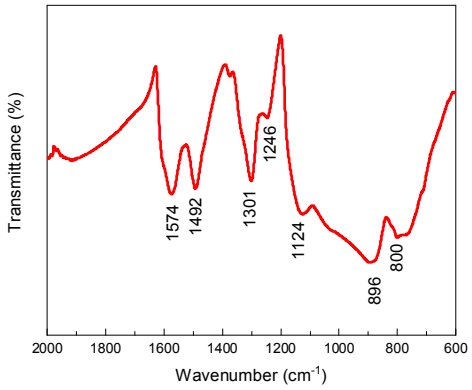

Figure 5*. FTIR spectra of PAni.*

UV-Vis spectrum further confirmed this polyaniline is identical to that of acid doped emeradine PAni salt as it exhibits peaks at around 430 nm and a free carrier tail at wavelength > 800 nm as shown in Figure 6.[19] This can be attributed to polaron-π^* transition and π-polaron transition, respectively. Also, the free carrier tail in the IR region indicates that PAni has an expanded "coil-like" conformation.[20]

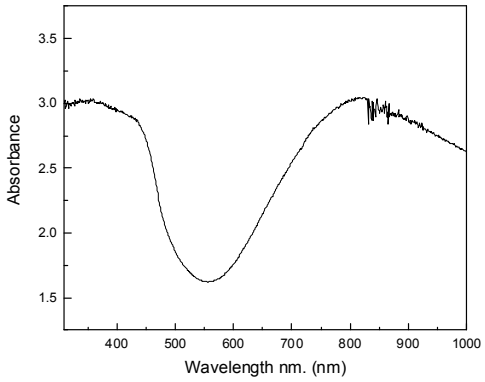

Figure 6*. UV-Vis spectra of PAni.*

Figure 7 and Figure 8 show SEM and TEM images of PAni. It consists of a hierarchical 3D porous foam-like network of nanofibers. This morphology is consistent with that obtained from bulk PAni synthesis.

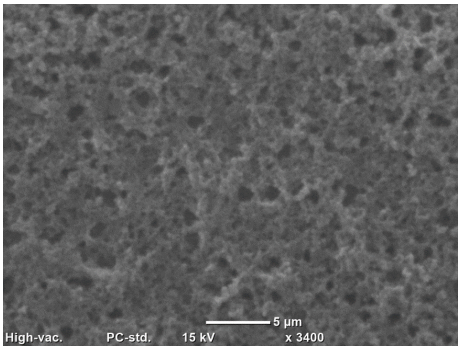

Figure 7*. SEM image of PAni.*

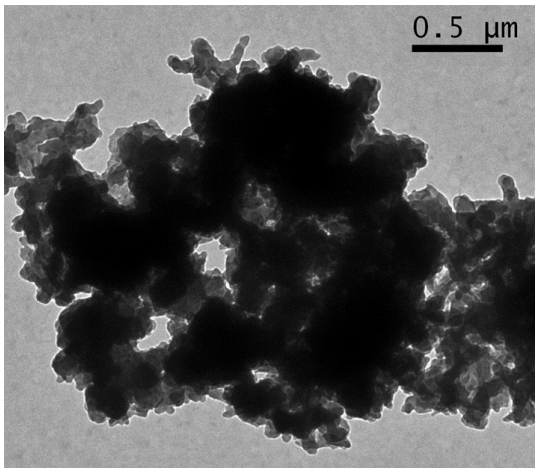

***Figure 8**. TEM image of PAni.*

Figure 9 presents the AFM image of the surface morphology of micro-reactive inkjet printed PAni. The RMS roughness of the thin film is 144 nm.

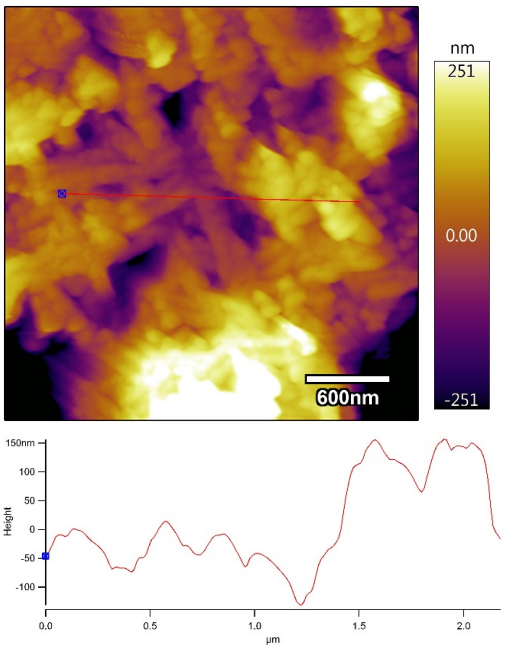

***Figure 9**. AFM image of PAni.*

Figure 10 demonstrates the XRD pattern of partly crystalline PAni film with a diffraction peak at 25.5^{o}, which corresponds to the cofacial stacking distance between the phenyl rings. Therefore, the π-π stacking is parallel to the film surface as the phenyl rings are normal to the film surface.[21]

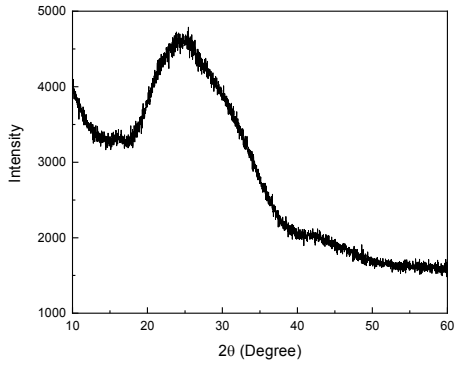

***Figure 10**. XRD pattern of PAni.*

Conclusion

In conclusion, we have developed an innovative method for the fabrication of patterned PAni with triton-X100 on glass substrates. Moreover, this versatile micro-reactive printing technique provides a new way of achieving patterned PAni other than using pre-synthesised and dispersed PAni nanoparticles. The fabrication of both films and arbitrary linear 2D structures has been demonstrated. The synthesized PAni has a porous morphology with conductivity of ~ 0.6 S cm^{-1}, significant higher than previous work with inkjet printed PAni, and approaching the value of bulk synthesized PAni. In addition, this simple and innovative method for synthesising polyaniline is expected to expand the scope of applications to a wider range of material synthesis at a micro-scale level, while keeping the intrinsic advantages of multi-material deposition of inkjet printing.

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