Supporting information

The In Situ Synthesis of Conductive Polyaniline Patterns Using Micro-reactive Inkjet Printing

Mei Ying Teo, Logan Stuart, Harish Devaraj, Cody Yang Liu, Kean C. Aw, Jonathan Stringer*

Department of Mechanical Engineering, The University of Auckland, Symonds Street, Auckland 1010, New Zealand.

Corresponding Author

* Email: j.stringer@auckland.ac.nz; Phone: +64 9 923 70

Experimental Section

Device preparation and operation. The inkjet dispensing setup consists of drive electronics (JetDrive III CT-MC3-4, Microfab Technologies, Plano, TX, USA), pressure controller (CT-PT-4, Microfab Technologies), rotary vane pump RZ 6 (Vacuubrand, Germany), two piezoelectric printheads (MJ-ATP-01, 60 µm diameter, Microfab Technologies), LED, Supereyes B008 USB portable digital microscope and Basler ace acA640-120gm camera. All the images are subsequently analyzed using ImageJ. Also, stainless steel stands, laser cut acrylic parts and 3D printed PLA parts were used to mount various components (camera, LED and printheads) and align them with respect to each other. A high resolution 2D motorized stage (Suruga Seiki PG650-L05AG-E1) with a microcontroller (Arduino Mega 2560) powered via a USB connection and external power supply is positioned underneath the dispensing setup for patterning. The GUI was developed in LabVIEW software (National Instruments Corp., Austin, Texas, USA) that allows user to input G code for controlling the linear stages' movements to form different patterns on the substrates.

Materials and Methods. For the synthesis of conductive polymer PANI, aniline monomer (ACS reagent, ≥ 99.5 %) , phytic acid (50 %, w/w in water) and ammonium persulfate (ACS reagent, ≥ 98 %) were used. For ink preparation, ethylene glycol (purity 99%) and surfactant Triton X-100 were used. All chemicals were purchased from Sigma-Aldrich and used as received without any treatment. Deionized water (DI) was used as solvent for both the inks throughout the experiments.

Inks preparation. Ink A comprising of 0.45 ml aniline (monomer) and 0.64 ml phytic acid (dopant) were dissolved in 2 ml DI water. Ink B containing 0.4 g ammonium persulfate (oxidant), 0.18 ml ethylene glycol (viscosity modifier) were vigorously mixed in 2 ml DI water. In addition, 1 wt % of Triton X-100 was added to the Ink B. Both inks were filtered through 0.45 µm filter to remove large particles. The viscosities of the Ink A and Ink B solutions were measured using a rheometer (Brookfields LV-DV3T) under couette flow. The surface tension of the inks were measured using a torsion balance, Model 'OS' (White Electrical Instrument Co. Ltd., North Malvern, UK). The contact angle was determined by the sessile drop method (CAM100, KSV Instruments, Helsinki, Finland).

Synthesis of PANI by Micro-reactive Inkjet Printing. Both Ink A and Ink B were loaded into separate reservoirs connected to the piezoelectric printheads. Drive electronics (JetDrive III CT-MC3-4, Microfab Technologies, Plano, TX, USA) assisted by Jetserver software (Microfab Technologies, Plano, TX, USA) is used to generate the electrical pulses required for the jetting of droplets A and droplets B. Meanwhile, a pressure controller (CT-PT-4, Microfab Technologies) and a rotary vane pump RZ 6 (Vacuubrand, Germany) is used to control the pressure during jetting of both Ink A and Ink B from the reservoirs while printing. A very small negative pressure (~8-10 mbar) is applied to prevent unwanted wetting of the printhead nozzle. Droplets are ejected from both nozzles and coalesced in mid-air to initialize the polymerization reaction before reaching the glass substrate. Generally, the droplet size is approximately equal to the nozzle size and in this study, two 60 µm diameter piezoelectric printheads (MJ-ATP-01, Microfab Technologies) are used to generate droplets.[27] However, it is possible to control the droplet size (within a defined range) by adjusting the electrical driving pulse used to form the droplets. 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; and then UV cleaned at 25°C for 10 min. Drop spacing of 160 µm was selected after optimizations. Then, the films were washed in a deionized water bath to remove excess acid and by-products from polymerization.

Characterization of the PANI films. The sheet resistance of the films were measured by four-point-probe method. The current and voltage were applied and measured using 4-wire sensing mode on a Keysight B2902A precision source/measure unit. Film thicknesses were determined using a Bruker Dektak XT. FTIR measurement was done on a Thermo Nicolet iS50 spectrometer (Thermo Fisher Scientific Co., USA). The FTIR spectra was acquired in the range of 400-4000 with a resolution of 4 cm^{-1} and averaged over 32 scans. Raman spectra was determined using Renishaw System 1000 Raman spectrometer, applying laser with a wavelength of 488 nm. The spectra was acquired in the range of 150 cm^{-1} to 2000 cm^{-1} by accumulating 5 scans. The Raman system was calibrated over the same scanning range using the 1086 cm^{-1} band of calcite prior to data acquisition. UV-Vis spectra was recorded on a Shimadzu UV-3600 plus spectrophotometer (Shimadzu Corp., Kyoto, Japan) and the background absorption of the glass substrate was excluded. SEM images were obtained using an analytical field emission SEM (Hitachi SU-70, Japan) operated at 5 kV. Samples were Pt-sputtered using Hitachi E-1045 ion sputter with Pt target and a current of 25 mA for 20 s. AFM images were taken in tapping mode using a silicon probe with a tip radius of <10 nm, f ~ 300 kHz and k 40 N m^{-1} (BudgetSensors, Sofia, Bulgaria) under MFP-3D Origin AFM (Oxford Instruments, Santa Barbara, CA). The set point amplitude was adjusted to 80% of the free air amplitude (1 V) and the integral gain was set to 10 for the approach and varied during imaging to obtain a good trace or retrace. The scan rate was kept at 1 Hz to obtain optimum images. Optical microscope image was obtained using a CETI TRITON II materials microscope. XRD pattern was obtained using Ultima IV Rigaku XRD system with Cu-Kα radiation (λ=1.54 Å) operated at 40 kV and 30 mA at room temperature. The XRD spectra were measured in the 2θ angular region between 5° and 60° with a step size of 0.02°.

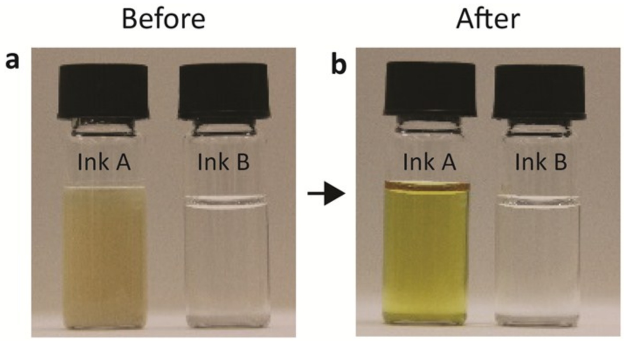

Fig. S1 Photograph of all five component materials dissolved in Ink A and Ink B. (a) Before filtration (b) After filtration.

Table S1 Ink properties.

Properties	Ink A	Ink B
Viscosity	1.98 cP	1.30 cP
Surface tension	56 mN/m	40 mN/m
Contact angle (glass)	$15.71^{\circ} \pm 2^{\circ}$	$11.07^{\circ} \pm 2^{\circ}$
Color -Before	Yellowish brown	Transparent
-After	Yellow	Transparent

Table S2 Comparison of the studies between the experimental factors and the electrical properties of inkjet printed PANI.

Printing technique	Ref.	Additional Info	Substrate	Number of layer	Resistance (Ω)	Resistivity (Ω cm)	Sheet resistance (Ω/□)	Conductivity (S cm^{-1})
Conventional inkjet	[4]	-	Standard paper	20	-	-	-	0.0004
	[30]	w/MWCNT	Photo paper	1	-	-	500	-
	[31]	-	PET	40	1.57 x 10^{6}	-	2480	0.0004
	[32]	-	Photo paper	4	-	-	22000	-
	[5]	-	Polyester	1	25000	-	-	-
	[33]	-	Polyimide	1	-	8 x 10^{5}	-	-
	[6]	-	Polyimide	3	-	990	-	-
	[34]	-	PET	1	-	-	531 x 10^{6}	4.5 x 10^{-5}
	[35]	nanowire	Transparency film	25	-	-	5000	-
	[36]	-	Polyimide	1	-	-	-	0.3
Single reactive inkjet	[23]	Soaked in aniline	Glossy paper	2	-	-	-	0.02
	[24]	Aniline vapor + HCl gas	PET	2	-	-	3800	4.8
Full reactive inkjet	[25]	-	Glossy photo paper	2	-	-	-	0.11
	[12]	-	Polyacrylonitrile textile	2	-	-	233	-
	[28]	-	Polyacrylonitrile textile	5	-	-	20	-
	Present work	-	Glass	1	-	-	9729	0.61

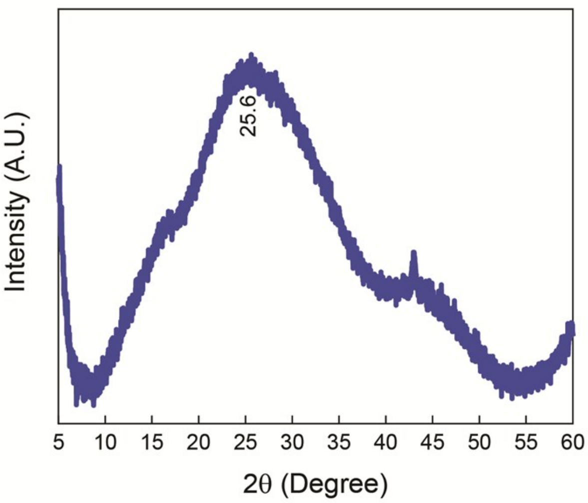

Fig. S2 XRD pattern of PANI.