Supporting Information

Electrohydrodynamic jet printed conducting polymer for enhanced chemiresistive gas sensors

Nhlakanipho Mkhize,*^a Krishnan Murugappan,*^{a,b} Martin R. Castell,^a and Harish Bhaskaran.^a

a. Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK.

b. Nanotechnology Research Laboratory, College of Engineering and Computer Science, The Australian National University ACT 2601, Australia.

*These authors contributed equally

Reaction of polyaniline and ammonia

The reaction mechanism of polyaniline with ammonia is well-known.¹ Figure S1 demonstrates how the doping of the emeraldine base form of polyaniline results the conductive emeraldine salt form. The acid anion creates a radical cations (polaron), with which the ammonia reacts during exposure.² In this work, when nitrogen is used to purge the vacuum chamber between ammonia exposure windows, the reacted ammonia is desorbed, resulting in baseline recovery.



Figure S1. Ammonia reaction with acid and ammonia. a) The protonation of polyaniline emeraldine base with acid results in the conductive green emeraldine salt. b) Ammonia reacts with this salt to revert to the base form, which is more resistive. In this work, HA = hydrochloric acid, camphorsulfonic acid and a 1:1 mixture of the two acids.

Electrohydrodynamic jet printing mechanism



Figure S2. Forces acting at capillary during electrohydrodynamic jet printing. The formation of the Taylor cone is the distinguishing point which allows for printing of features smaller than the nozzle diameter.

The mechanism behind electrohydrodynamic jet printing was first described by Taylor.³ When an electrical stress is applied to a liquid in a capillary, the meniscus deforms. When the stress is great enough, the surface tension of the liquid is overcome, and a jet is generated. The tangential stress deforms the meniscus, and the normal stress sustains the jet. Various other factors influence the jetting; including viscosity, frequency (if AC bias is applied), and nozzle diameter. Extensive work in understanding these parameters and more has been reported. ^{4–8}



Figure S3. Printed HCl doped polyaniline sensor on glass substrate. a) Unclear sensing results are obtained for this sensor, owing to the limited bridging shown in b) the SE micrograph. The large particle size of this ink, due to poor solubility, results in nozzle clogging.

The printing of HCl doped polyaniline was not remarkably successful on the glass substrate, even after numerous attempts. When initially checked, the above sample (Figure S3) was conductive and was thus used in the vacuum chamber. The sensing measured was negligible.

Solubility

Table S1. Summary of peak UV/Vis peak positions in different acid environments, before and afteraddition of non-ionic surfactant (Span[®] 80).

	Peak position (nm)									
Ink	HCI	HCL doped	CSA	CSA doped	Co-doped	Co-doped with				
	doped	with surfactant	doped	with surfactant		surfactant				
Peak 1	341	337	336	337	347	345				
Peak 2	416	416	410	410	416	416				
Peak 3	871	871	838	834	872	872				

To assess whether the addition of a surfactant would lead to the increased solubility of the polyaniline in solution, UV/Vis spectra were measured. Table S1 summarizes the peaks observed both before and after the addition of the surfactant. The three peaks (as observed in Figure S4) are much broader for the HCl doped and co-doped polyaniline than the CSA doped blend. This is due to the higher levels of aggregation. The addition of surfactant does not significantly affect the band positions nor bandwidth, this indicating that the aggregation is not molecular, but rather more clumping due to poor solubility. Whilst these insoluble clumps could be filtered, the resultant solution would be of a very low concentration, making sensing even harder. Therefore, it is more beneficial to break the clumps up by mechanical agitation and print the dispersion quickly to attain the highest concentration of polyaniline possible.



Figure S4. Normalized UV/Vis spectra of polyaniline suspensions in NMP. Both the HCl and co-doped polyaniline suspensions exhibit a redshift and a peak broadening in the NIR region, which is indicative of a large degree of aggregation. The more pronounced shoulder peak too at ca. 420 nm is evidence of larger particles. The $\Delta\lambda$ in the figure shows the red shift of the HCl doped and co-doped blends (33 nm shift).

Limit of detection

The limit of detection was determined using the equation

Limit of detection = $(3.3 \times SD)/s$

Where the SD and s are the standard deviation (at low concentrations) and the gradient of the linear regression fit, respectively. Table S2 summarizes the LOD values calculated for the printed sensors, where there is n/a, no sensing data was obtainable.

		Thin Film sensor			EHD Printed sensor		
	Substrate	HCI	Co- doped	CSA	HCI	Co- doped	CSA
Limit of detection	Glass	n/a	n/a	n/a	n/a	0.86	0.22
(ppm)	Flexible	NR	NR	NR	0.74	n/a	n/a

Table S2. Summary of LOD data for tested samples.

The standard exposure limit is 25 ppm. The best performing sensor is the CSA doped polyaniline sensor on glass. NR stands for No Recovery.



Figure S5. High resolution SEM images of CSA and co-doped polyaniline on both flexible and rigid substrates. The connectivity on the a) flexible substrate is insufficient to bridge the inter-electrode distance. There is clear electrode bridging on b) glass substrate, giving rise to detectable sensing. Similarly, for the c) co-doped flexible substrate, insufficient conducting pathways exist for effect sensing, whereas on the d) glass substrate, there are.



Figure S6. Optical microscope images of spun-coat polyaniline on silica. Spin-coating was performed on silica surfaces with co-doped (a, b), CSA doped (c, d) and HCl doped (e, f) polyaniline. The spin-coating was also performed at different rotational speeds (2000 & 3000 rpm) to ascertain whether a change in velocity would be beneficial to film formation.

Figure S6 shows the result of spin coating polyaniline onto cleaned silica surfaces. It is evident from these images that poor film formation occurs, because of poor adhesion. The advantage of EHD printing is that it offers focused deposition rather than the diffuse deposition of dropcasting or spin-coating. This is especially important as the Polyaniline is insoluble in any solvent system. Even with higher solubility (thus smaller particle size) seen with the CSA doped (Figure S6 c, d), there is still segregation during drying. This would not be observed if the ink were completely dissolved.

References

- Dhawan, S. K.; Kumar, D.; Ram, M. K.; Chandra, S.; Trivedi, D. . Application of Conducting Polyaniline as Sensor Material for Ammonia. *Sensors Actuators B. Chem.* **1997**, 40, 99–103.
- (2) Kebiche, H.; Debarnot, D.; Merzouki, A.; Poncin-Epaillard, F.; Haddaoui, N. Relationship between Ammonia Sensing Properties of Polyaniline Nanostructures and Their Deposition and Synthesis Methods. *Anal. Chim. Acta* **2012**, *737*, 64–71.
- (3) Taylor, G. Electrically Driven Jets. *Proceeds R. Soc. London A* **1969**, *313*, 453–475.
- Yu, M.; Ahn, K. H.; Lee, S. J. Design Optimization of Ink in Electrohydrodynamic Jet Printing: Effect of Viscoelasticity on the Formation of Taylor Cone Jet. *Mater. Des.* 2016, *89*, 109–115.
- (5) Lee, A.; Jin, H.; Dang, H. W.; Choi, K. H.; Ahn, K. H. Optimization of Experimental Parameters to Determine the Jetting Regimes in Electrohydrodynamic Printing. *Langmuir* 2013, 29 (44), 13630–13639.
- (6) Choi, K.-H.; Ali, K.; Rahman, K. A Study of the Dependence of Electrohydrodynamic Jetting on the Process Parameters and Liquid Physical Properties. *Chinese J. Phys.* 2014, 52 (2), 799–815.
- (7) Fernández de la Mora, J. The Fluid Dynamics of Taylor Cones. Annu. Rev. Fluid Mech.
 2007, 39 (1), 217–243.
- (8) Onses, M. S.; Sutanto, E.; Ferreira, P. M.; Alleyne, A. G.; Rogers, J. A. Mechanisms, Capabilities, and Applications of High-Resolution Electrohydrodynamic Jet Printing. *Small* **2015**, No. 34, 4237–4266.