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Fabrication of chemical sensors using inkjet printing and application to gas detection

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Keywords

Fabrication, chemical, sensors, using, inkjet, printing, application, gas, detection

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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Fabrication of chemical sensors using inkjet printing and application to gas detection

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Abstract—This work describes the fabrication of gas sensors using inkjet printing. Sensors were constructed by building up a film of sensing material, such as polyaniline, from aqueous nanoparticulate dispersions. These films were printed over patterned silver interdigitated array designs for the purposes of conductimetric analysis. Unlike screen printing or lithography, inkjet printing does not require stencils or masks, therefore allowing rapid design and prototyping. For this study, polyaniline and modified polyaniline sensors were inkjet printed and assessed for the purposes of gas sensing applications, specifically hydrogen sulfide monitoring.

I. Introduction

Polyaniline (PANI) is a conducting polymer that has been widely employed for gas sensing. However, one of the major problems is the lack of processability which makes mass-production of devices based on the polymer difficult. The polymer only dissolves in certain organic solvents (e.g. n-methylpyrrolidone) which are environmentally unfriendly and expensive. The solution to this problem is to use aqueous dispersions of polyaniline nanoparticles (nanoPANI) in the fabrication of devices. In this form, PANI is highly processable and a number of techniques can be used to fabricate sensors and other devices, one such technique is inkjet printing. In recent times, inkjet printing has been shown to be a versatile technique for depositing a range of different materials for a range of different applications. Previously, dispersions of nanoPANI were characterised and optimised for inkjet printing applications [1].

PANI exists in a number of oxidation states; the most relevant to this study is the emeraldine form. This state can be further subdivided into emeraldine salt (conductive) and emeraldine base (non-conductive) forms. Gas-phase sensing using PANI typically involves monitoring the changes in conductivity of the polymer on exposure to the analyte of interest. Scheme 1 shows a simplified reaction scheme of emeraldine conversion while Figure 1 gives examples of the inkjet printed sensors.
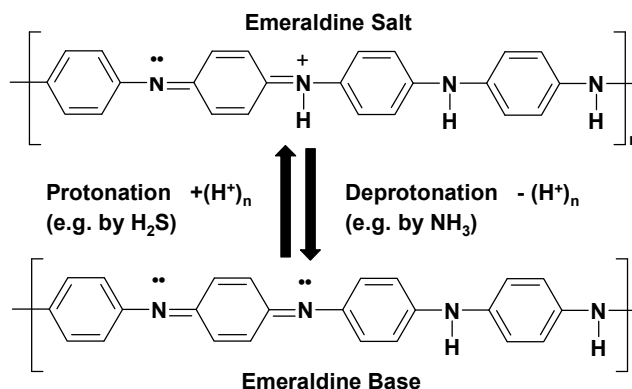
Scheme 1. Conversion of emeraldine salt to emeraldine base and vice versa.

Previously, we have shown that sensors fabricated from inkjet printed nanoPANI can be employed for the analysis of ammonia in both the aqueous [2] and gaseous phase [3]. In this work, modified sensors are employed for the detection of different analytes, specifically nanoPANI-$CuCl_2$ for the detection of hydrogen sulfide gas (H_2S).
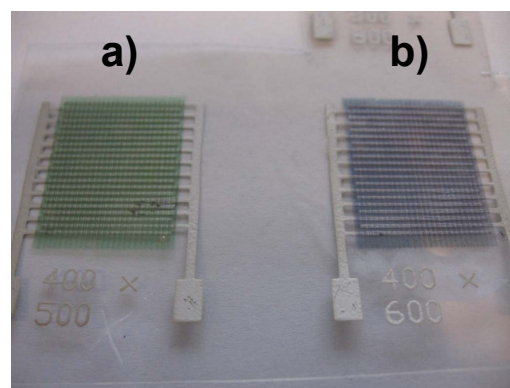
Figure 1. Examples of an unmodified (a) and $CuCl_2$ treated (b) inkjet printed nanoPANI sensor.

II. Experimental

A. Reagents

The fabrication of polyaniline nanoparticle dispersions has been detailed previously [1]. In brief, 0.6 ml of freshly distilled aniline (Sigma Aldrich), 3.4 g dodecylbenzenesulfonic acid (DBSA, TCI) and 0.36 g ammonium persulfate (APS, Sigma) were mixed in 40 ml deionised water and stirred for 2.5 hours. During this time a dark green viscous solution was formed. The solution was then centrifuged at 5000 rpm for 30 minutes prior to dialysis against 0.05 M sodium dodecyl sulfate (SDS) for 2 days to remove excess DBSA and APS. 0.375 M copper chloride solution for printing was prepared by dissolving 6.34g of copper chloride dihydrate (Sigma Aldrich) in 100 ml water.

B. Preparation of inkjet printed electrodes

Silver and carbon interdigitated electrodes (IDAs) were prepared using screen printing on a DEK 247 printer using commercial silver and carbon paste inks (Acheson). Electrode patterns were drawn using AutoCAD (Autodesk). The electrodes were printed to a polyethylene terephthalate (PET) substrate and then heat treated at 150°C for 30 minutes. Inkjet printing was performed on Dimatix 2811 and 2831 inkjet printers (FujiFilm Dimatix, Inc.). The piezoelectric nozzle voltages were optimised before each print run but were generally of the order of 16 – 20 V for nanoPANI solutions. The aqueous $CuCl_2$ solutions were printed using the standard printer settings (16 V). Unless otherwise stated, the films were printed using 40 μm resolution (dot spacing = 250 dpcm). All printing solutions were passed through 0.45 μm filters when filling the inkjet cartridges to remove larger particulate matter. The cartridges used for printing were MEMS-based, with 16 nozzles (20 μm diameter) spaced at 254 μm. The droplet volume is quoted at being 10 pL. Standard (unmodified) nanoPANI sensors were fabricated by printing 10 layers of the nanoPANI solution on to the interdigitated pattern. Base-treated nanoPANI sensors were briefly dipped into 0.1 M NaOH solution to convert them to the emeraldine base form. NanoPANI-$CuCl_2$ films were prepared by printing alternate layers of nanoPANI and $CuCl_2$ solutions (5 layers of each).

C. Gas analysis

Conductimetric readings of the IDA sensors were performed using a multi-channel CHI1000 potentiostat in two electrode mode. A potential (+0.1 V, unless otherwise stated) was applied across the electrode and measured current plotted against time. Ammonia gas was provided by Scott Specialty gases, hydrogen sulfide and all other gases were provided by Sigma Aldrich. Headspace gas analysis was performed using either a custom built 4 L gas box or a 3 L box equipped with a mixing fan (General Monitors). The gas of interest was introduced to the chamber through a septum using a gas syringe set to the appropriate volume. Venting the gas involved opening the chamber and flushing with compressed air.

III. Results and Discussion

A. Optimisation of printing parameters

In previous work, inkjet printing was performed using standard desktop printers (e.g. Epson C46/48) with modified cartridges [2,3]. Printing parameters such as piezoelectric nozzle voltage, clean cycles, etc. were all factory set and could not be modified – severely restricting the flexibility. On the other hand, numerous printing parameters can be adjusted on the Dimatix system, allowing for the optimisation of inkjet parameters for printing different formulations. A full scale optimisation for a particular fluid is a time consuming process worthy of a full study in itself therefore a shortened description is given here.
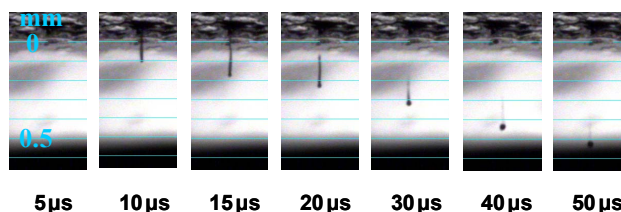
Figure 2. Evolution of inkjet printed droplet of nanoPANI solution over time.

Figure 2 shows the evolution of a droplet of nanoPANI suspension during the printing cycle, taken with the "drop-watcher" camera on the printer. Droplets are ejected with a tail that should ideally draw into the main body of the drop throughout the process, failure to do so will result in satellite droplets and a reduction in print quality. This generally indicates a too high nozzle voltage or excessive surface tension (can be reduced using surfactants). In the worst cases, droplets completely shatter – resulting in many small droplets, akin to shotgun pellets, leading to a severe reduction in quality.
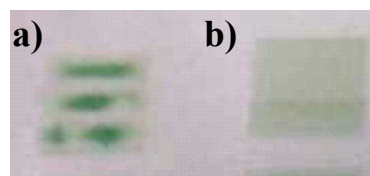
Figure 3. Effect of print resolution on print quality. a) 1 layer printed at 20 μm and 5 layers at 40 μm.

Another important consideration is the compatibility of the printed solution and substrate. For example, printing hydrophilic solutions to excessively hydrophobic surfaces will lead to broken films, as the solution forms high contact angle drops on instead of homogenous layers. Conversely, if the surface is too hydrophilic, drops will spread out of the printed area, destroying the pattern. Another consideration is print resolution; greater resolution allows for finer patterns and larger quantities of material to be printed. However,

pooling can occur resulting in an uneven print. Figure 3 shows the effect of printing one layer at 20 μm resolution (a) and five layers at 40 μm (b). The 20 μm print suffers from the effects of pooling leading to an inhomogeneous film while the 40 μm results in considerably greater uniformity.
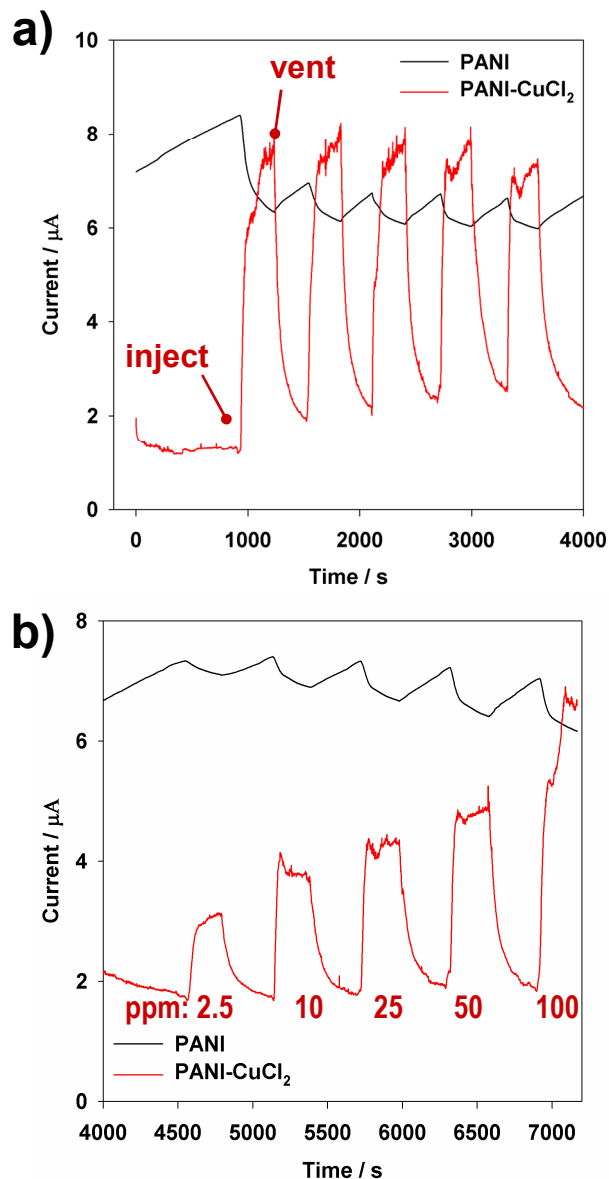
B. NanoPANI-CuCl₂ sensor:

Previously, Virji *et al.* had used polyaniline films doped with CuCl₂ and observed a drop of resistance on exposure to H₂S [4]. Polyaniline-copper acetate films were found to give a fast response to H₂S but did not recover, making them suitable for dosimeter type devices [5]. In this case, modification of the polyaniline with copper chloride appears to have the effect of switching the polymer from the emeraldine salt form to one of the non-conductive forms, presumably emeraldine base, as the measured current was initially three to four orders of magnitude below an unmodified nanoPANI electrode. The nanoPANI-CuCl₂ sensors appeared blue in colour due to a combination the base form and the presence of the copper (II) salt. A quantity of the copper complexes with the amine and imine groups in the PANI and on exposure to H₂S, the complexed copper bonds with the sulfide [4] – the released protons resulting in increased conductivity of the film (see Scheme 1).

Initial experiments were conducted using nanoPANI-CuCl₂ printed to both carbon and silver interdigitated electrodes. Sensors based on the carbon electrodes were found to behave in a similar dosimeter fashion to that observed by Virji *et al* [5]. The sensors printed to silver IDAs displayed markedly different behaviour with rapid response and recovery to hydrogen sulfide. The reason for this is presumably due to an effect of the silver substrate. Silver is rapidly tarnished by hydrogen sulfide in a reaction that also leads to the release of protons and forms non-conductive silver sulfide (a common problem with silver-based contacts). This effect, combined with the irreversible reactions of H₂S with silver and copper chloride within the active layer limits the lifetime of the device at present, though response single or short-term use sensors can be readily fabricated.

To fully assess the effect of hydrogen sulfide on the response of the nanoPANI-CuCl₂ sensor, the current-time responses were compared with those simultaneously acquired for unmodified nanoPANI (emeraldine salt form) and base-treated nanoPANI (emeraldine base form), both on silver IDAs. This was possible using the multiplex function on the CHI1000 potentiostat. On initial exposure to 100 ppm hydrogen sulfide, both the base-treated nanoPANI and nanoPANI-CuCl₂ sensors displayed a sharp increase in measured current (~ four orders of magnitude), indicating that the polyaniline had been protonated by the gas to the emeraldine salt form. This effect was largely irreversible with both types of sensor retaining the improved conductivity. The unmodified nanoPANI sensor showed a much more modest increase, less than one order of magnitude and slowly recovered once the gas was removed. On subsequent injections of H₂S, the CuCl₂-modified sensor

displayed markedly different behaviour: rapid increases in measured current on injection followed by a rapid decrease when the chamber was vented. In comparison, the unmodified nanoPANI sensor displayed a much weaker and slower response. This can be seen in Figure 4 (a) where the results obtained for five sequential 100 ppm aliquots of H₂S are given for both types of sensor. After each injection the sensors are allowed stabilise over 5 minutes, before the chamber is vented for an additional 5 minutes. Unusually, the nanoPANI sensor displays a slight fall on exposure to the gas, followed by a slight rise when vented.

Figure 4. Current/time plots obtained for nanoPANI and nanoPANI-CuCl₂ sensor response to hydrogen sulfide; (a) 5 sequential 100 ppm inject and vent cycles, (b) inject/vent cycles of increasing concentrations of H₂S. Both sensors consisted of a silver-based IDA electrode.

Figure 4 (b) gives the response of nanoPANI and nanoPANI-CuCl₂ sensors to increasing concentrations of hydrogen sulfide in the analytically important sub 100 ppm region. Again, the rapid response and recovery of the device can be observed. Figure 5 shows the calibration plots obtained for both types of sensor. Current values were sampled 180s after each injection and the background current was subtracted from the data. It can be seen that for the nanoPANI-CuCl₂ sensor, a linear response is observed between 10 and 100 ppm. The sensor also has no difficulty detected concentrations down to 2.5 ppm (given by squares) though was below the linear portion of the plot.

$$y = 0.0309x + 1.746$$
$$r^2 = 0.9878$$
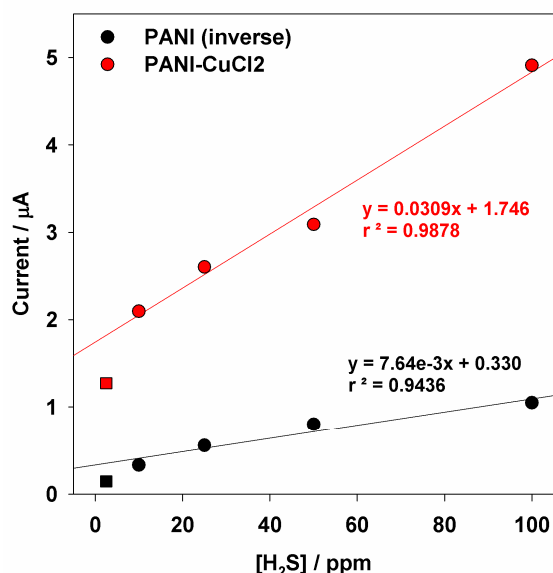
$$y = 7.64e\text{-}3x + 0.330$$
$$r^2 = 0.9436$$

Figure 5. Calibration plots obtained for the data given in Figure 4 (b). Circles show linear response between 10 and 100 ppm. Squares show response to 2.5 ppm H₂S (not included in linear regression). Current values taken 180 s after gas injection.

IV. CONCLUSION

The inkjet fabrication and application of a nanoPANI sensor modified with the transition metal salt CuCl₂ to the detection of hydrogen sulfide gas is described. Initially, the optimisation of the inkjet printing parameters is performed for the printing solutions prior to inkjet printing of the nanoPANI and nanoPANI-CuCl₂ sensors. The sensors were employed for the detection of hydrogen sulfide with the nanoPANI-CuCl₂ giving a linear response to quantities between 10 and 100 ppm. This sensor could be applied as a disposable, short use sensor. Current work involves improving the long term stability of the sensor material and assessing the effects of potentially interfering species.

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