RESEARCH ONLINE

University of Wollongong
Research Online

Faculty of Science - Papers (Archive)

Faculty of Science, Medicine and Health

2010

Fabrication of polyaniline-based gas sensors using piezoelectric inkjet and screen printing for the detection of hydrogen sulfide

Karl H. Crowley
null@uow.edu.au

A Morrin

Roderick L. Shepherd
University of Wollongong, rods@uow.edu.au

Marc in het Panhuis
University of Wollongong, panhuis@uow.edu.au

Gordon G. Wallace
University of Wollongong, gwallace@uow.edu.au

See next page for additional authors

Publication Details

Crowley, K. H., Morrin, A., Shepherd, R. L., in het Panhuis, M., Wallace, G. G., Smyth, M. R. & Killard, A. J. (2010). Fabrication of polyaniline-based gas sensors using piezoelectric inkjet and screen printing for the detection of hydrogen sulfide. IEEE Sensors Journal, 10 (9), 1419-1426.

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

RESEARCH ONLINE

Fabrication of polyaniline-based gas sensors using piezoelectric inkjet and screen printing for the detection of hydrogen sulfide

Abstract

This work describes a fully printable polyaniline-copper (II) chloride sensor for the detection of hydrogen sulfide gas. The sensing device is composed of screen printed silver interdigitated electrode (IDE) on a flexible PET substrate with inkjet printed layers of polyaniline and copper (II) chloride. The sensor is employed as a chemiresistor with changes in measured current being correlated with concentration. On exposure to hydrogen sulfide, 2.5 ppmv (parts per million by volume) is clearly detectable with a linear relationship between measured current and concentration over the 10-100 ppmv region. The detection mechanism is discussed with respect to the hydrogen sulfide response, the choice of electrode materials in addition to UV-vis and surface enhanced Raman spectroscopy (SERS) characterization. © 2006 IEEE.

Keywords

hydrogen, detection, printing, screen, sulfide, inkjet, fabrication, piezoelectric, sensors, gas, polyaniline

Disciplines

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

Publication Details

Crowley, K. H., Morrin, A., Shepherd, R. L., in het Panhuis, M., Wallace, G. G., Smyth, M. R. & Killard, A. J. (2010). Fabrication of polyaniline-based gas sensors using piezoelectric inkjet and screen printing for the detection of hydrogen sulfide. IEEE Sensors Journal, 10 (9), 1419-1426.

Authors

Karl H. Crowley, A Morrin, Roderick L. Shepherd, Marc in het Panhuis, Gordon G. Wallace, Malcolm R. Smyth, and Anthony J. Killard

This journal article is available at Research Online: http://ro.uow.edu.au/scipapers/582

Fabrication of Polyaniline-Based Gas Sensors Using Piezoelectric Inkjet and Screen Printing for the Detection of Hydrogen Sulfide

Karl Crowley, Aoife Morrin, Roderick L. Shepherd, Marc in het Panhuis, Gordon G. Wallace, Malcolm R. Smyth, and Anthony J. Killard

***Abstract*—This work describes a fully printable polyaniline-copper (II) chloride sensor for the detection of hydrogen sulfide gas. The sensing device is composed of screen printed silver interdigitated electrode (IDE) on a flexible PET substrate with inkjet printed layers of polyaniline and copper (II) chloride. The sensor is employed as a chemiresistor with changes in measured current being correlated with concentration. On exposure to hydrogen sulfide, 2.5 ppmv (parts per million by volume) is clearly detectable with a linear relationship between measured current and concentration over the 10–100 ppmv region. The detection mechanism is discussed with respect to the hydrogen sulfide response, the choice of electrode materials in addition to UV-vis and surface enhanced Raman spectroscopy (SERS) characterization.**

***Index Terms*—Gas sensor, hydrogen sulfide, inkjet printing, polyaniline.**

I. Introduction

THE detection of toxic gases has been a major focus of sensor research in recent years. Many natural and industrial processes release gases that can cause immediate damage or long term human health effects. Hydrogen sulfide is often produced during the petrochemical process [1], is present in natural gas and is often released in large quantities during volcanic activity [2]. It is denser than air, a fact which can allow it to accumulate in sheltered and underground areas such as sewers or mines. In addition, though pungent smelling, prolonged exposure to even relatively low quantities results in the loss of sense of smell [3]. For these reasons, development of simple, low cost sensors is desirable for a variety of environmental and health and safety applications.

Inkjet printing has been utilized as a means to fabricate sensors and other functional devices in whole or in combination with other production methodologies [4]. To date, a wide variety of materials (polymers, inorganic polymers, etc.) can be utilized and printed to a range of substrates [5]. Compared with mask-based methods such as screen printing and photolithography, patterns can be rapidly designed, prototyped and changed as printing is done directly from software such as AutoCAD. Another major advantage that inkjet printing has over the mask-based methods is the noncontact nature of the process. This prevents possible cross-contamination or damage to underlying structures when printing multiple layers. Though inkjet cannot compete at present with traditional silicon chip fabrication when it comes to complex computer components, the technique can be used to mass produce simple circuits and devices at low cost. Many different devices have been fabricated in this way; Yoshioka and Jabbour utilized a thermal inkjet printer to fabricate OLEDs based on poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) [6]. Kim *et al.* fabricated a transistor based upon inkjet printed inorganic oxides [7] while Eom and coworkers developed and characterized solar cells based upon modified PEDOT-PSS films [8].

Organic conducting polymers have been widely employed for the detection of gaseous species. One of the most widely used has been polyaniline, which has been commonly applied as a gas sensing material [9]. A particular advantage of conducting polymer-based sensors is the relative ease with which they can be modified either to improve sensitivity and selectivity or allow new species to be detected. The sensing behavior of polyaniline has been modified through the application of blends such as polyaniline/carboxylated polyvinyl chloride (for the detection of ammonia down to 1 ppm) [10], or a Nafion/polyaniline/urease sensor for the detection of urea in solution [11]. Polyaniline composites have also been fabricated through the addition of materials; e.g., carbon nanotubes for the detection of carbon monoxide [12] and alcohols [13] and titanium dioxide particles for the detection of ammonia and carbon monoxide [14]. A relatively simple means of modification is simply treating the polyaniline to chemical modification with inorganic salts. Virji *et al.* utilized polyaniline nanofibers modified with copper (II) chloride to fabricate a dosimeter for the detection of hydrogen sulfide [15].

Manuscript received October 20, 2009; revised December 10, 2009; accepted February 14, 2010. Date of publication June 07, 2010; date of current version July 14, 2010. This work was supported in part by Enterprise Ireland (PC/2006/113, PC/2007/138). This is an expanded paper from the IEEE SENSORS 2008 Conference. An earlier version of this paper was published in its proceedings. The associate editor coordinating the review of this paper and approving it for publication was Dr. M. Abedin.

K. Crowley, A. Morrin, M. R. Smyth, and A. J. Killard are with the Sensors and Separations Group, School of Chemical Sciences, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland (e-mail: karl.crowley@dcu.ie; aoife.morrin@dcu.ie; malcolm.smyth@dcu.ie; tony.killard@dcu.ie).

R. Shepherd and G. G. Wallace are with the ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Squires Way, Fairy Meadow, NSW 2519, Australia (e-mail: rods@uow.edu.au; gwallace@uow.edu.au).

M. in het Panhuisis with the Soft Materials Group, School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia (e-mail: panhuis@uow.edu.au).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/JSEN.2010.2044996

1530-437X/$26.00 © 2010 IEEE

Previously, we have reported results obtained for inkjet printed PANI sensors for the detection of ammonia in gaseous and aqueous media [16], [17]. These sensors were printed using commercially available desktop printers (e.g., piezoelectric Epson inkjets). In this paper, the modified polyaniline sensors were fabricated using a Dimatix materials printer (Fujifilm Dimatix, Inc.). Printing parameters were optimized to enhance the quality of printed material. The sensors composed of polyaniline nanoparticles were modified with inkjet printed copper chloride and were assessed for the detection of hydrogen sulfide. Preliminary data was presented previously [18] and in this work, the effect of electrode material was assessed and found to have a major impact on the behavior of the sensor. This will be discussed with reference to the electrical properties of the conducting polymer which has been characterized with respect to UV-vis and surface enhanced Raman spectroscopy (SERS) and possible mechanisms will be detailed.

II. Experimental

A. Formulation of Inks

The fabrication of polyaniline nanoparticle dispersions has been detailed previously [19], [20]. 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 h. During this time, a dark green viscous solution was formed. The solution was then centrifuged at 5000 rpm for 30 min prior to dialysis against 0.05 M sodium dodecyl sulfate (SDS) for 2 days to remove excess APS and unreacted aniline. 0.375 M copper chloride solution for printing was prepared by dissolving 6.34 g of copper chloride dihydrate (Sigma Aldrich) in 100 ml water.

B. Preparation of PANI and PANI-$CuCl_2$ Sensors

Silver and carbon interdigitated electrodes (IDEs) were prepared using screen printing on a DEK 248 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 optimized before each print run but were generally of the order of 16–26 V for PANI solutions. The aqueous $\mathrm{CuCl_2}$ 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 Dimatix 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. PANI-$\mathrm{CuCl_2}$ films were prepared by printing alternate layers of PANI and $\mathrm{CuCl_2}$ solutions (five layers of each). Base-treated PANI sensors were prepared by briefly dipping unmodified PANI sensors into 0.1 M NaOH solution to convert them to the emeraldine base form.

C. Spectroscopic Characterization

UV-visible spectroscopy was performed using a Lambda 900 spectrometer (Perkin Elmer Inc.). Solutions were diluted as appropriate and absorption spectra obtained between 325 and 1100 nm using quartz cuvettes. Absorption spectra of the sensors were also obtained by directly by placing the sensor electrode (on the PET substrate) in the cuvette holder. In this case, a background spectrum was obtained of a bare (as prepared) IDE electrode on PET. Obtaining spectra in this way appeared to prevent interference from the opaque silver IDE pattern. Raman spectroscopy was carried out on the printed films using a RamanStation 400 F (PerkinElmer Inc.) equipped with a 785 nm (near infrared) 350 mW laser. Measurements were taken of the sensor films directly with no sample preparation or treatment. In each case, five exposures of 20 s each were performed for each sample. Surface enhanced Raman spectroscopy (SERS) was performed by collecting spectra of the films in contact with the silver electrode substrate. Optical microscopy images of the sensor films were collected using the onboard CCD camera of the Raman spectrometer.

D. Sensor Operation

Electrical measurements were performed with a CHI1000 potentiostat (CH Instruments, Inc.) in two electrode mode. The experiments were performed by applying a fixed potential of +0.1 V across the sensor (using the "amperometric i-t curve" setting) and measuring the current against time. Gas detection experiments were performed by sealing the sensor within a 4 L chamber with mixing fan and introducing fixed volumes of pure (>99.5%) hydrogen sulfide gas (Sigma Aldrich Company). The gas was vented when required by opening the chamber. Humidity measurements were performed by placing sensors within a MTCL 350 environmental chamber (Tas UK, Ltd.). The connections with the potentiostat were made through a sealable cable port.

III. Results and Discussion

A. PANI Modification With $CuCl_2$

Modification of the polyaniline with copper chloride appears to have the effect of switching the polymer from the emeraldine salt (ES) form to one of the non-conductive forms, presumably the emeraldine base (EB) or pernigraniline base (PB), as the measured current was initially three to four orders of magnitude below an unmodified PANI electrode. This was shown previously by Dimitriev, who demonstrated that doping an emeraldine base polyaniline film with copper chloride leads to partial formation of the pernigraniline base form [21]. Fig. 1 shows images of unmodified and modified PANI sensors. The unmodified PANI is visually green and displays a granular appearance under the microscope. On modifying with aqueous $\mathrm{CuCl_2}$, the film appeared blue in color due to a combination the base forms and the presence of the copper (II) salt. In addition, the silver digits can be seen to have taken on a brown color, pointing to the reduction of the copper ions to metallic copper. After repeated exposure to hydrogen sulfide gas, the film gradually becomes gray-brown and opaque, due to formation of copper sulfides. The electrode digits had also lost the brown coloration due to metallic copper.

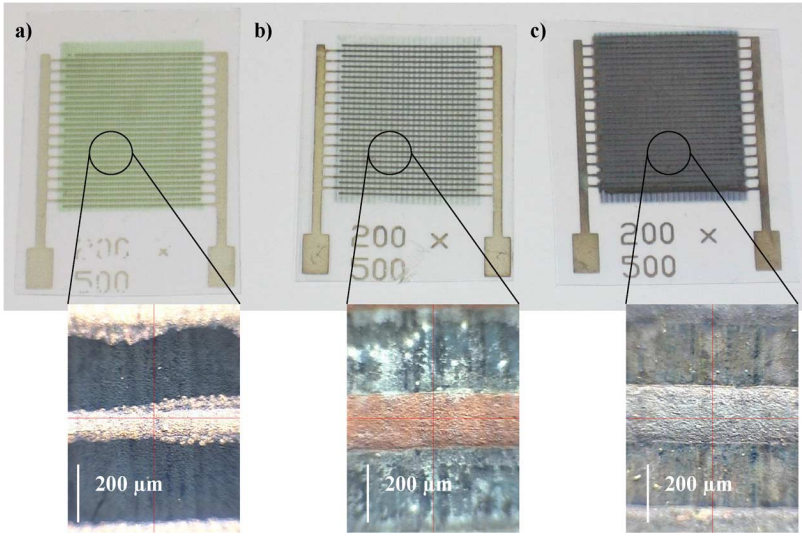

Fig. 1. Interdigitated electrodes with inkjet printed films of (a) PANI, (b) PANI-$CuCl_2$ (pre H_2S exposure), and (c) PANI-$CuCl_2$ (post H_2S exposure). Insets compare optical microscopy of the electrode digits and sensor films.

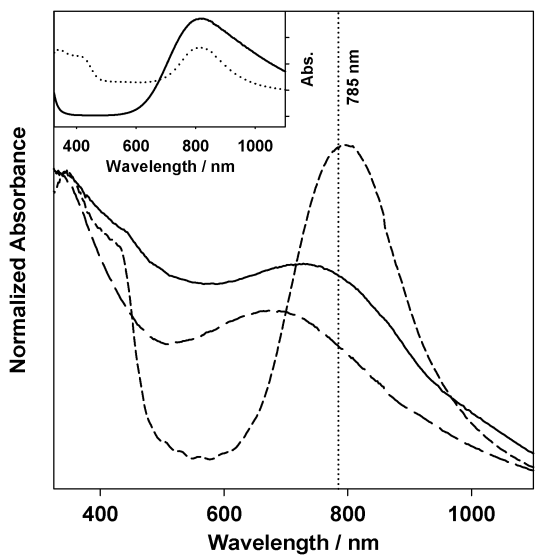

Fig. 2. UV-Vis-NIR absorption spectra obtained for IDE sensors on PET. Solid line: PANI-$CuCl_2$ sensor, wide dash: PANI EB sensor, short dash: PANI ES sensor. The position of the 785 nm Raman excitation line is given by the dotted line. The inset shows the absorption spectra obtained for the ink solutions. Solid line: polyaniline formulation (1:50 dilution in H_2O), dotted line: 0.125 M $CuCl_2$ in water (1:3 dilution).

These effects will be analyzed in greater detail in the following sections.

B. Spectroscopic Characterization

1) UV-Vis Spectroscopy of PANI-$CuCl_2$ Films: For a greater understanding of the behavior of the PANI-$CuCl_2$ films, spectroscopic characterization was performed. Initially, UV-vis spectroscopy was performed on printed films with no IDE pattern. However, the electrode material has a noticeable effect on the film behavior and this method was therefore not suitable. Therefore, spectra were acquired of the IDE sensors directly with a bare IDE pattern used as the background scan. Despite the narrow pitch of the electrode spacing, satisfactory spectra were obtained in each case. Fig. 2 shows the UV-vis plot obtained for a freshly prepared PANI-$CuCl_2$ sensor in addition to PANI ES and PANI EB sensors (it was not possible to obtain a spectrum for a PANI-$CuCl_2$ sensor post H_2S exposure due to its high opacity). The plots were normalized with respect to the maxima of the 325–350 nm band. The inset of Fig. 2 shows the spectra obtained for the ink formulations used (diluted as necessary). The polyaniline nanoparticle dispersions gave the same spectra to those obtained previously [19], with characteristic features present for emeraldine salt. The copper chloride solution gave a spectrum with a broad feature centred at about 800 nm.

The PANI ES sensor film yielded a similar spectrum as the ink formulation, with the $\pi - \pi^*$ band at 350 nm, a π-polaron band at 430 nm and the polaron band at 800 nm. The PANI EB sensor film displayed absorption bands at 325 nm (assigned to the $\pi - \pi^*$ transition) and a broad feature at 682 nm due to the localized quinoid structure of EB [22]. Printed PANI-$CuCl_2$ sensors displayed a similar spectrum to PANI EB, this suggests that the $CuCl_2$ modification shifted the sensor into the EB form. There was no evidence of pernigraniline formation (shifting of the band at 682 nm to shorter wavelengths), which has been noted previously for Cu^{2+} interaction with PANI EB in n-methyl-2-pyrrolidinone [23], indeed the band was actually shifted to a longer wavelength (722 nm).

2) Raman Spectroscopy of PANI-$CuCl_2$ Films: For a more detailed assessment of the effect of copper chloride modification on polyaniline, Raman spectroscopy was employed in the analysis of the sensor films. Raman is a vibrational spectroscopic technique, similar to infrared (IR) spectroscopy. However, it does not suffer from water interference and requires little sample preparation, both of which are often issues for IR. Previously, Raman has been widely employed for the analysis of the different oxidation states of various conducting polymers, including polyaniline [24]. Baibarac *et al.* examined ES and EB forms of polyaniline on a variety of metallic substrates (Ag, Au, Cu) using SERS with a 1064 nm laser [25]. In this case, spectra of the sensors were acquired using a 785 nm laser. From the main plot in Fig. 2, it can be seen that excitation at this wavelength was in resonance with the polaron/quinoid bands. Spectra

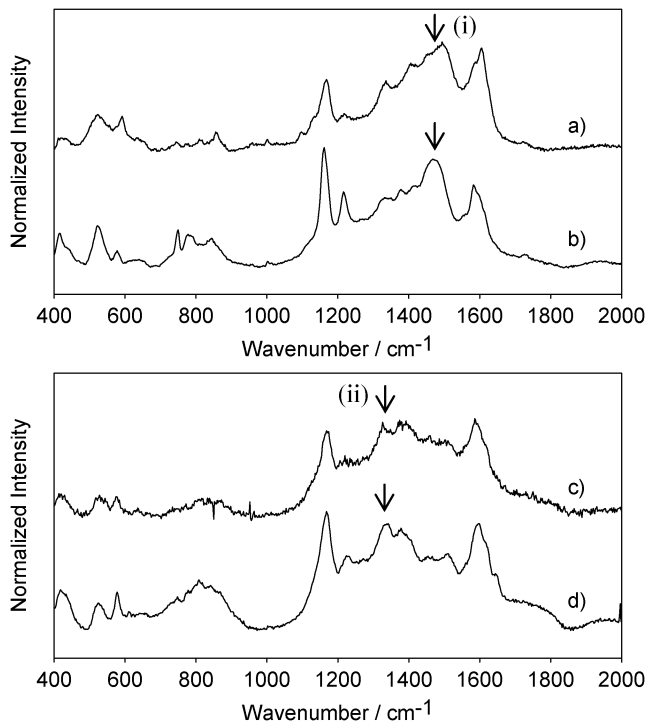

Fig. 3. Raman Spectra obtained for PANI-$CuCl_2$ and unmodified PANI sensors. (a) PANI-$CuCl_2$ (pre H_2S exposure), (b) base-treated PANI (emeraldine base), c) PANI-$CuCl_2$ (post H_2S exposure), and (d) unmodified PANI (emeraldine salt). Highlighted bands: (i) $C = N$ stretch [25], [26] and (ii) protonated structure [25].

TABLE I
MAJOR RAMAN BAND ASSIGNMENTS OBSERVED FOR POLYANLINE AND POLYANILINE-COPPER CHLORIDE (PRE AND POST HYDROGEN SULFIDE EXPOSURE)

Assignment [25,26]	*PANI-$CuCl_2$ (pre)*	*PANI-EB*	*PANI-$CuCl_2$ (post)*	*PANI-ES*
C=C, C-C stretching	1606	1586	1588	1600
C=N stretch	1498	~1480	~1500	~1500
Protonated structure	1380-1330 weak	1380-1330 weak	1380-1330	1380-1330
C-N stretch	~1230	1218	~1230 weak	~1236
C-H bending	1172	1162	1174	1172

were acquired for the portion of the films that were in contact with the silver electrodes. This was for two reasons; to examine the nature of the underlying electrode substrate and to utilize the SERS effect to improve spectral intensity. SERS spectra were obtained for PANI-$CuCl_2$ sensors before and after exposure to hydrogen sulfide. Spectra were also obtained for unmodified PANI ES and PANI EB on silver IDEs for comparison. Although the differences in band intensity between ES and EB were relatively subtle [26], differences were present that allowed the assignment of the correct state of the polymer.

Fig. 3 shows the SERS spectra obtained for the different sensors and the assignment of the relevant bands is given in Table I. Despite the difference in excitation wavelength, the spectra obtained for the unmodified ES and EB forms of the polymer were broadly in agreement with those obtained by Baibarac *et al.* on silver substrates [25]. Prior to hydrogen sulfide exposure the main distinguishing feature of the PANI-$CuCl_2$ sensor was a broad band at approximately 1500 cm^{-1} [band (i), Fig. 3(a)], assigned to the $C = N$ stretch [26]. This band was also present for emeraldine base [Fig. 3(b)] and was found to be very intense for silver substrates [25], confirming the assertion that $CuCl_2$ modification causes the polymer to shift to the nonconducting emeraldine base form. There are no obvious bands directly due to copper chloride modification or generated sulfides in either of the PANI-$CuCl_2$ films. However, evidence of copper was present. On the unexposed PANI-$CuCl_2$ film the C-N stretch at 1220 cm^{-1} was diminished with respect to the C-H bending band at 1160 cm^{-1}, compared to the PANI EB film. This would be expected for PANI EB on a copper substrate and would support the visual evidence that copper metal had formed on the silver IDE digits. The sharp band at 1608 cm^{-1} present for the $CuCl_2$-modified film and greatly diminished for the PANI EB film of silver also supports this assertion.

Attempts at acquiring bands from a PANI-$CuCl_2$ sensor after exposure to hydrogen sulfide were problematic. As noted in the last section, exposure to H_2S caused the modified films to turn grey-brown and opaque, pointing to the formation of Cu_2S [27]. In a recent Raman study on copper sulfides, Munce *et al.* noted that Raman spectra of chalcocite (Cu_2S) have not been widely reported due to a variety of factors including its metallic character and fluorescence [28]. The weakening of the bands attributable to PANI would therefore be due to interference caused by fluorescence from the copper sulfide in the film and this results in the noisy spectrum given in Fig. 3(c). Nevertheless, the weakened spectrum displays similar character to the emeraldine salt spectrum [Fig. 3(d)] with similar band wavenumbers and relative intensities. The main features of these spectra compared with Fig. 3(a) and (b) are the diminished 1500 cm^{-1} $C = N$ stretching band, with an increase in the broad feature between 1330 and 1380 cm^{-1} [band (ii), Fig. 3(c) and (d)] assigned to the protonated structure [25].

C. Hydrogen Sulfide Detection With PANI-$CuCl_2$ Sensor

To fully assess the effect of hydrogen sulfide on the response of the PANI-$CuCl_2$ carbon IDE, the current-time responses were compared with those simultaneously acquired for unmodified PANI (emeraldine salt form) and base-treated PANI (emeraldine base form). Responses of the PANI-$CuCl_2$ layers to hydrogen sulfide gas were obtained using both carbon and silver IDEs. On initial exposure to 100 parts per million by volume (ppmv) hydrogen sulfide, both the base-treated PANI and PANI-$CuCl_2$ sensors displayed a sharp increase in measured current (~four orders of magnitude), indicating that the polyaniline had been protonated by the gas to the conducing emeraldine salt form. This effect was largely irreversible with both types of sensor retaining the improved measured current. The unmodified PANI sensor showed a much more modest increase in current, less than one order of magnitude and slowly recovered once the gas was removed. On subsequent injections of H_2S, the $CuCl_2$-modified sensor displayed markedly different behavior: rapid increases in measured current on injection followed by a rapid decrease when the chamber was vented. In comparison, the unmodified PANI sensor displayed a much weaker and slower response. These unmodified electrodes displayed a sharp irreversible drop in measured current,

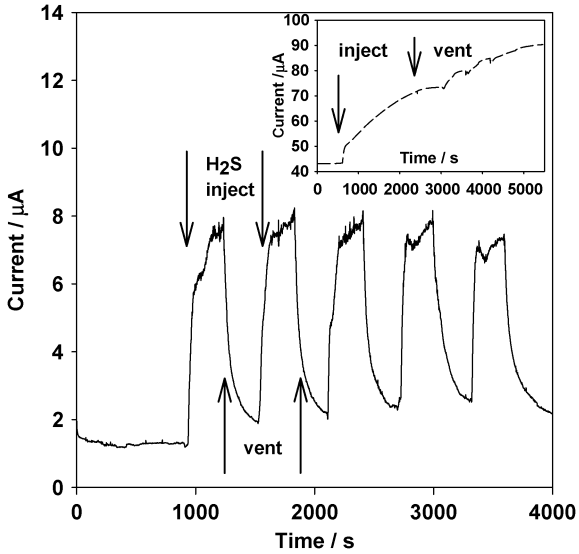

Fig. 4. Response of PANI-$CuCl_2$ to hydrogen sulfide gas. Main plot shows response of sensor using silver IDE to injection/vent cycles of 100 ppmv hydrogen sulfide. Inset shows response using carbon IDE.

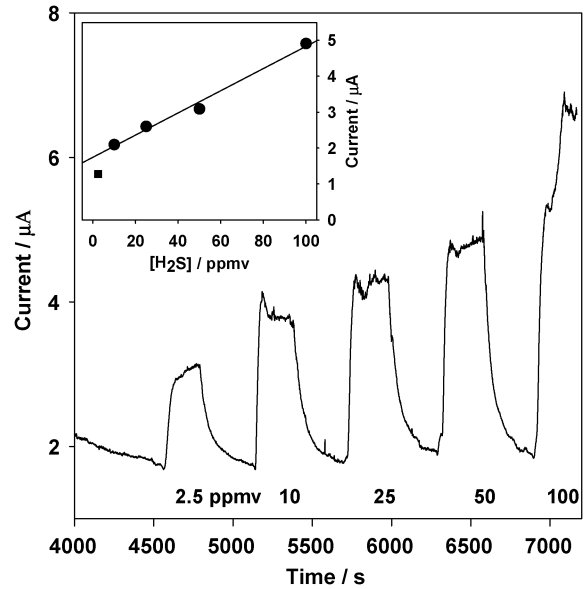

Fig. 5. Current-time transient obtained for a PANI-$CuCl_2$ sensor (silver IDE) on exposure to increasing concentrations of hydrogen sulfide gas. Inset shows the calibration plot obtained (data sampled 180 s after each injection).

due to the immediate formation of black silver sulfide on the electrode digits.

Preliminary results had shown that the behavior of PANI-$CuCl_2$ sensors to hydrogen sulfide exposure was heavily dependent on the electrode material. PANI-$CuCl_2$ sensors were printed on both carbon and silver IDEs. Fig. 4 (inset) shows the response obtained when a PANI-$CuCl_2$ film on a carbon IDE is exposed to inject/vent cycles of 100 ppmv H_2S. A steady, irreversible increase in current was observed while the sensor was exposed to H_2S and levelled off to a plateau when the chamber was vented; in this case no recovery was observed. This dosimeter style behavior was in agreement with that observed previously for a polyaniline nanofiber/copper chloride sensor [15]. The main plot of Fig. 4 shows the response obtained when a PANI-$CuCl_2$ film on a silver IDE is exposed to inject/vent cycles of 100 ppmv H_2S. In this case, a reproducible response and recovery profile is observed for five subsequent inject/vent cycles with a value of 7.33 ± 0.15 μA $(n = 5)$ measured for 100 ppmv hydrogen sulfide, 180 s after the gas was injected. Good sensor recovery was also observed during venting with the transient approaching the baseline after 600 s. Fig. 5 shows the result of increasing concentrations of hydrogen sulfide on sensor response. In this case a steady increase is observed with hydrogen sulfide concentration. Again, the current was sampled three minutes after each exposure to hydrogen sulfide and the resulting calibration plot is presented in the inset of Fig. 5. A linear response between hydrogen sulfide concentration and current is obtained between 10 and 100 ppmv ($y = 0.0309x + 1.75$, $R^2 = 0.9878$), though concentrations down to 2.5 ppmv were clearly visible.

Sensors based on inkjet printed polyaniline have previously been found to show only very slight variations in measured current with changes in ambient humidity [16]. In this study, a PANI-$CuCl_2$ sensor was compared in parallel with an unmodified PANI-ES sensor. The temperature was held at 20 °C and the

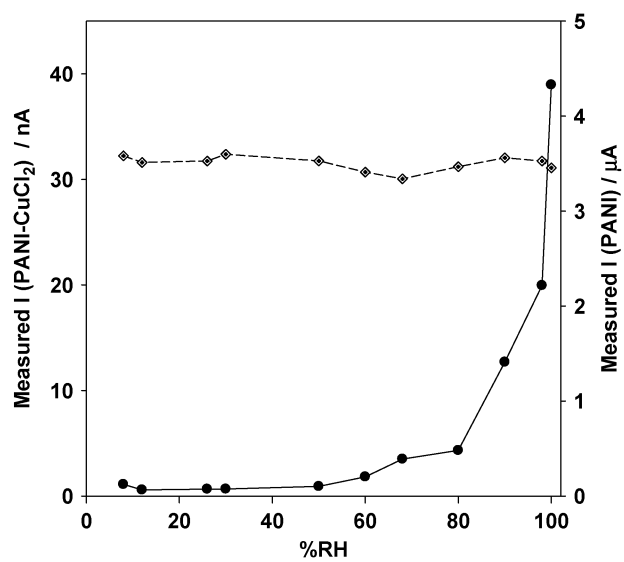

Fig. 6. The effect of relative humidity on sensor response. Solid line: PANI-$CuCl_2$ sensor, dashed line: unmodified PANI sensor.

relative humidity was increased from 8 to 100%. The changes in measured current with %RH are given in Fig. 6. As before, the PANI sensor was found to display no major changes over the full range $(3.50 \pm 0.077\ \mu A)$. The PANI-$CuCl_2$ sensor is relatively stable below 50 %RH (0.791 ± 0.22 nA). At higher %RH, the measured current increases gradually between 50% and 80% before a sharp increase between 80 and 100%. This effect was reversible with the measured current dropping back once the humidity was lowered. The increase in measured current is possibly due to water condensing on the sensor; increasing the ionic mobility of the free Cu^{2+} and Cl^- ions, leading to greater ionic conductivity within the film. Operating the sensor under drier conditions is clearly desirable, the interference from humidity becoming significant above 80 %RH.

Previously, we have shown that printed polyaniline sensors are very responsive to ammonia gas [16] and tests were performed to assess the effect of several potentially interfering species. For freshly prepared PANI-$CuCl_2$ sensors, exposures to 100 ppmv concentrations of nitric oxide, carbon monoxide and ammonia were found to result in no measurable response. The lack of response due to ammonia in particular is interesting but not unexpected: the ammonia interaction with polyaniline is due to conversion of the emeraldine salt form to the base form [16], [17]. As noted from the Raman spectra presented earlier, the PANI-$CuCl_2$ is initially in the emeraldine base form. After the initial exposure to hydrogen sulfide (and the resulting conversion of emeraldine base to salt), ammonia may be expected to interfere. Further testing will be required to assess if this is indeed the case.

D. Mechanism

The behavior of the PANI-$CuCl_2$ sensor is considerably more complicated than the relatively simply doping/dedoping behavior observed for unmodified PANI in the presence of ammonia. The chemistry of copper sulfides is extremely complex [28] and beyond the scope of this paper, instead a simplified treatment will be given here. The response obtained on the PANI-$CuCl_2$ silver electrode sensor to hydrogen sulfide implies that another process is occurring, one that does not occur for PANI-$CuCl_2$ on a carbon IDE. In the case of the carbon IDE, the copper chloride does not react with the electrode digits and the copper II complexes with the PANI as described previously [15], resulting in the conversion of emeraldine salt to the emeraldine base as noted earlier. On exposure to H_2S, the copper preferentially bounds to the sulfide, releasing hydrogen chloride. The acid then protonates the PANI film leading to formation of emeraldine salt (as observed in the Raman spectra in Fig. 3) and a corresponding increase in conductivity, as given below

$$CuCl_2 + H_2S \rightarrow CuS + 2HCl \tag{1}$$

$$PANI(EB) + HCl \rightarrow PANI(ES)H^+ + Cl^-. \tag{2}$$

This leads to an irreversible increase in conductivity as given in the inset of Fig. 4. It was noted earlier that when printing $CuCl_2$ over the silver IDE, the digits can be seen to darken to a brown/black color (Fig. 1), implying the formation of metallic copper. This is due to the oxidation of silver and reduction of copper in the presence of chloride ions. Some formation of copper (I) chloride and silver chloride may also occur

$$CuCl_2 + 2Ag \rightarrow Cu(s) + 2AgCl \tag{3}$$

$$CuCl_2 + Ag \rightarrow CuCl + AgCl. \tag{4}$$

Surprisingly, the reaction of silver with the chloride does not result in the same irreversible effect on sensor conductivity as was noted for the sulfide reaction at the unmodified PANI silver IDE: the sensors retain the ability to conduct. When the sensor is exposed to hydrogen sulfide gas, the metallic copper is oxidized to copper sulfide with a release of protons and electrons. Additionally, the silver chloride also reacts, releasing HCl. Visually, the modified PANI film turns from blue (complexed copper II) to grey-brown; indicating the formation of a copper-rich sulfide (approximate stoichiometry of Cu_2S) [27]

$$H_2S + 2Cu(s) \rightarrow Cu_2S + H_2S + H^+ + e^- \tag{5}$$

$$H_2S + 2AgCl \rightarrow Ag_2S + 2HCl. \tag{6}$$

The generation of protons converts the PANI polymer from emeraldine base to the salt form; as is the case for sensors with carbon-based IDEs. The release of electrons result in the rapid, sharp current observed for PANI-$CuCl_2$ Ag IDEs. When the gas is removed, the release of electrons rapidly halts, and the measured current drops back to the baseline. However, unlike the protonation and deprotonation reactions of emeraldine PANI, the conversion to metal sulfides are irreversible. Over time, this mechanism requires that the free copper will be consumed and experimentally, this was found to be the case as the response of the electrode was observed to drop steadily after several exposures as all of the free copper is oxidized to copper sulfide. Recovering the sensor is problematic. Previously, we have used a temperature-based recovery to remove ammonia from PANI electrodes [16]. Higher temperatures were found to shorten the sensor operating lifetime. When applied to a spent PANI-$CuCl_2$ sensor, heating at 70 °C was found to return the sensor to a blue-green color. However, this did not result in restoration of the sensing behavior of the films. In this case, the color change through heating was due to changes in the copper sulfide structure. Silvester *et al.* observed that copper sulfide sols were initially golden brown in color (broadly due to Cu_2S) and turned green (formation of covellite, CuS) in a temperature dependent reaction [27].

IV. Conclusion

The fabrication and operation of a printed polyaniline/$CuCl_2$ sensor is demonstrated for hydrogen sulfide detection. Spectroscopic characterization shows that modification with copper chloride causes the polyaniline film to shift from the conductive emeraldine salt form to the nonconducting emeraldine base form. In addition, copper metal was found to form on the silver digits of the interdigitated electrodes. Exposure of the sensors to hydrogen sulfide gas in the low ppmv region resulted in rapid response and recovery profiles as opposed to the dosimetric behavior observed for PANI-$CuCl_2$ films on inert carbon electrodes. The sensors could be employed for short term analyses but as the free copper and silver in the film is converted to sulfides, the sensor response diminishes. Humidity was found to interfere in the sensor response, however this effect could potentially be eliminated through use of hydrophobic membranes. Further work would be required to determine whether a fully reversible sensor based on this material is possible. Though silver has shown to be critical for the sensing properties of the film, the use of carbon or other chemically inert materials could be employed for the contacts and conductive tracks not in contact with the film. Chemical or electrochemical methods of reducing the copper and silver sulfides could also be investigated.

REFERENCES

[1] M. A. Mehlman, "Dangerous and cancer-causing properties of products and chemicals in the oil refining and petrochemical industry. 4. Human health and environmental hazards resulting from oil and oil products," *J. Clean Technol. Environm. Sci.*, vol. 1, pp. 103–121, Apr. 1991.

[2] A. Hansell and C. Oppenheimer, "Health hazards from volcanic gases: A systematic literature review," *Arch. Environ. Health*, vol. 59, pp. 628–639, Dec. 2004.

[3] [Online]. Available: http://www.cdc.gov/niosh/npg/npgd0337.html

[4] E. Fisslthaler, A. Bluemel, K. Landfester, U. Scherf, and E. J. W. List, "Printing functional nanostructures: A novel route towards nanostructuring of organic electronic devices via soft embossing, inkjet printing and colloidal self assembly of semiconducting polymer nanospheres," *Soft Matter*, vol. 4, pp. 2448–2453, 2008.

[5] E. Tekin, P. J. Smith, and U. S. Schubert, "Inkjet printing as a deposition and patterning tool for polymers and inorganic particles," *Soft Matter*, vol. 4, pp. 703–713, 2008.

[6] Y. Yoshioka and G. E. Jabbour, "Desktop inkjet printer as a tool to print conducting polymers," *Synth. Met.*, vol. 156, pp. 779–783, Jun. 1, 2006.

[7] G. H. Kim, H. S. Kim, H. S. Shin, B. D. Ahn, K. H. Kim, and H. J. Kim, "Inkjet-printed InGaZnO thin film transistor," in *Proc. 1st Int. Conf. Microelectron. Plasma Technol., Thin Solid Films*, 2009, pp. 4007–4010.

[8] S. H. Eom, S. Senthilarasu, P. Uthirakumar, S. C. Yoon, J. Lim, C. Lee, H. S. Lim, J. Lee, and S. Lee, "Polymer solar cells based on inkjet-printed PEDOT:PSS layer," *Organic Electron.*, vol. 10, pp. 536–542, May 2009.

[9] U. Lange, N. V. Roznyatouskaya, and V. M. Mirsky, "Conducting polymers in chemical sensors and arrays," *Anal. Chim. Acta*, vol. 614, pp. 1–26, Apr. 28, 2008.

[10] V. Singh, S. Mohan, G. Singh, P. C. Pandey, and R. Prakash, "Synthesis and characterization of polyaniline-carboxylated PVC composites: Application in development of ammonia sensor," *Sens. Actuators B-Chemical*, vol. 132, pp. 99–106, May 28, 2008.

[11] W. J. Cho and H. J. Huang, "An amperometric urea biosensor based on a polyaniline-perfluorosulfonated ionomer composite electrode," *Anal. Chem.*, vol. 70, pp. 3946–3951, Sep. 15, 1998.

[12] Y. Wanna, N. Srisukhumbowornchai, A. Tuantranont, A. Wisitsoraat, N. Thavarungkul, and P. Singjai, "The effect of carbon nanotube dispersion on CO gas sensing characteristics of polyaniline gas sensor," in *Proc. Symp. Opt. Spectroscopic Tech. Int. Con. Mater. Adv. Technol. (ICMAT 2005); J. Nanosci. Nanotechnol.*, 2006, pp. 3893–3896.

[13] W. R. Small and M. I. H. Panhuis, "Inkjet printing of transparent, electrically conducting single-waited carbon-nanotube composites," *Small*, vol. 3, pp. 1500–1503, Sep. 2007.

[14] H. Tai, Y. Jiang, G. Xie, J. Yu, and X. Chen, "Fabrication and gas sensitivity of polyaniline-titanium dioxide nanocomposite thin film," *Sens. Actuators B-Chem.*, vol. 125, pp. 644–650, Aug. 8, 2007.

[15] S. Virji, J. D. Fowler, C. O. Baker, J. X. Huang, R. B. Kaner, and B. H. Weiller, "Polyaniline manofiber composites with metal salts: Chemical sensors for hydrogen sulfide," *Small*, vol. 1, pp. 624–627, May 2005.

[16] K. Crowley, A. Morrin, A. Hernandez, E. O'Malley, P. G. Whitten, G. G. Wallace, M. R. Smyth, and A. J. Killard, "Fabrication of an ammonia gas sensor using inkjet-printed polyaniline nanoparticles," *Talanta*, vol. 77, pp. 710–717, Dec. 15, 2008.

[17] K. Crowley, E. O'Malley, A. Morrin, M. R. Smyth, and A. J. Killard, "An aqueous ammonia sensor based on an inkjet-printed polyaniline nanoparticle-modified electrode," *Analyst*, vol. 133, pp. 391–399, 2008.

[18] K. Crowley, A. Morrin, M. R. Smyth, A. J. Killard, R. Shepherd, M. in het Panhuis, and G. G. Wallace, "Fabrication of chemical sensors using inkjet printing and application to gas detection," in *Proc. 7th IEEE Sensors Conf.*, Leece, Italy, Oct. 26–29 , 2008, vol. 1, pp. 13–16.

[19] O. Ngamna, A. Morrin, A. J. Killard, S. E. Moulton, M. R. Smyth, and G. G. Wallace, "Inkjet printable polyaniline nanoformulations," *Langmuir*, vol. 23, pp. 8569–8574, Jul. 31, 2007.

[20] A. Morrin, O. Ngamna, E. O'Malley, N. Kent, S. E. Moulton, G. G. Wallace, M. R. Smyth, and A. J. Killard, "The fabrication and characterization of inkjet-printed polyaniline nanoparticle films," *Electrochim. Acta*, vol. 53, pp. 5092–5099, Jun. 30, 2008.

[21] O. P. Dimitriev, "Doping of polyaniline by transition-metal salts," *Macromolecules*, vol. 37, pp. 3388–3395, May 4, 2004.

[22] K. Lee, A. J. Heeger, and Y. Cao, "Reflectance spectra of polyaniline," *Synth. Met.*, vol. 72, pp. 25–34, Apr. 15, 1995.

[23] C. M. S. Izumi, A. M. D. C. Ferreira, V. R. L. Constantino, and M. L. A. Temperini, "Studies on the interaction of emeraldine base polyaniline with Cu(II), Fe(III), and Zn(II) ions in solutions and films," *Macromolecules*, vol. 40, pp. 3204–3212, May 1, 2007.

[24] M. C. Bernard and A. H.-L. Goff, "Quantitative characterization of polyaniline films using Raman spectroscopy I: Polaron lattice and bipolaron," *Electrochim. Acta*, vol. 52, pp. 595–603, Oct. 25, 2006.

[25] M. Baibarac, M. Cochet, M. Lapkowski, L. Mihut, S. Lefrant, and I. Baltog, "SERS spectra of polyaniline thin films deposited on rough Ag, Au and Cu. Polymer film thickness and roughness parameter dependence of SERS spectra," *Synth. Met.*, vol. 96, pp. 63–70, Jul. 15, 1998.

[26] S. Quillard, G. Louarn, S. Lefrant, and A. G. Macdiarmid, "Vibrational analysis of polyaniline—A comparative-study of leucoemeraldine, emeraldine, and pernigraniline bases," *Phys. Rev. B*, vol. 50, pp. 12496–12508, Nov. 1, 1994.

[27] E. J. Silvester, F. Grieser, B. A. Sexton, and T. W. Healy, "Spectroscopic studies on copper sulfide sols," *Langmuir*, vol. 7, pp. 2917–2922, Dec. 1991.

[28] C. G. Munce, G. K. Parker, S. A. Holt, and G. A. Hope, "A Raman spectroelectrochemical investigation of chemical bath deposited CuxS thin films and their modification," *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, vol. 295, pp. 152–158, Mar. 1, 2007.

Karl Crowley received the B.Sc. degree in physics and chemistry in 1998 and the Ph.D. degree in analytical and materials chemistry in 2003 from the Dublin Institute of Technology, Dublin, Ireland.

He is a Research Fellow at Dublin City University specializing in sensors and printed electronics. Previously, he has worked on wireless sensor networks, smart packaging and electrochemical and colorimetric sensors. A major focus of late has been in the commercialization of these devices. His current interests are in the development of new materials for gas sensors applied to industrial and biomedical analysis in addition to fabrication methodologies with inkjet, screen and other printing technologies.

Aoife Morrin received the Primary degree in applied sciences (chemistry and mathematics) in 2000 and the Ph.D. degree specializing in the application of conducting polymers in chemical- and biosensor applications from the Dublin Institute of Technology (DIT), Dublin, Ireland.

She is a Lecturer of Analytical Chemistry at Dublin City University. She has continued her research career at Dublin City University and has spent time in international research laboratories including Inverness Medical (Scotland), now Johnson & Johnson, a clinical diagnostics company, the University of the Western Cape (South Africa), and the Intelligent Polymer Research Institute (IPRI), Wollongong, Australia. Her research is currently in the area of electroanalytical device development for sensor and separations applications, using electroactive polymer nanomaterials and composites thereof, where improved performance is being demonstrated due to induced novel nanostructures in bulk material and tailored composite formulations.

Roderick L. Shepherd received the B.Env.Sc. (Hons.) and Ph.D. degrees from the University of Wollongong, Wollongong, N.S.W., Australia.

He is currently a Research Fellow at the Intelligent Polymer Research Institute, University of Wollongong. His research interests include chemical sensors, inherently conducting polymers, colorimetric optical sensors, robotics, electrochromics, and wireless sensor networking.

Marc in het Panhuis received the Chemical Engineering degree from the University of Twente, Enschede, The Netherlands, and the Ph.D. degree in physics from the University of Dublin, Trinity College, Dublin, Ireland.

He has worked in Chemistry and Physics Departments in Ireland, the U.K., and the U.S. before joining the University of Wollongong, Wollongong, Australia, in 2006. He is an Australian Research Council Future Fellow, Head of the Soft Materials Group, and a Chief Investigator in the ARC Centre of Excellence for Electromaterials Science. His main focus is to combine biopolymers with conducting fillers into soft biocompatible materials for biomedical applications.

Gordon G. Wallace is currently Director of the Intelligent Polymer Research Institute and Executive Research Director of the ARC Centre of Excellence for Electromaterials Science. His research interests include organic conductors, nanomaterials and electrochemical probe methods of analysis and the use of these in the development of Intelligent Polymer Systems. A current focus involves the use of these tools and materials in developing biocommunications from the molecular to skeletal domains in order to improve human performance via medical bionics.

Dr. Wallace was elected as a Fellow of the Australian Academy of Science in 2007 and the Australian Academy of Technological Sciences and Engineering in 2003. He was elected as a Fellow of the Institute of Physics (U.K.) in 2004. He is a Fellow of the Royal Australian Chemical Institute (RACI). In 2009, he was awarded a Life Time Achievement Award by SPIE in recognition of his sustained contributions to the development of smart materials. He received the RACI HG Smith Prize in 2008 and was named as NSW Scientist of the Year (Chemistry Category).

Malcolm R. Smyth received the B.Sc. degree from Queen's University of Belfast, Belfast, Ireland, in 1972, the Ph.D. degree in analytical chemistry from the University of London, London, U.K. in 1976, and the D.Sc. degree from Queen's University of Belfast in 1992.

He was appointed Professor of Chemistry in 1992 and Dean of the Faculty of Science and Health at Dublin City University in 1995.

Dr. Smyth is a Fellow of both the Royal Society of Chemistry and the Institute of Chemistry of Ireland. He received the Royal Society of Chemistry (RSC) Award in Chemical Analysis and Instrumentation for 1995, and the SAC Gold Medal for Analytical Chemistry in 1999 from the Analytical Division of the RSC.

Anthony J. Killard received the B.A. degree (Mod) from Trinity College Dublin, Dublin, Ireland, in 1993 and the Ph.D. degree in biotechnology at Dublin City University, Dublin, in 1998.

Currently, he is Principal Investigator at the Biomedical Diagnostics Institute and National Centre for Sensor Research, Dublin City University.