Dye-doped organically modified silica glass for fluorescence based carbon dioxide gas detection

C. Malins and B. D. MacCraith*

Biomedical and Environmental Sensor Technology Centre, School of Physical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland. E-mail: bdm@physics.dcu.ie

The sol–gel process was used to prepare organically modified silica glass in which the fluorescent pH-sensitive reagent 1-hydroxypyrene-3,6,8-trisulfonate is entrapped. An ion-pair approach was used to incorporate the hydrophilic dye in the hydrophobic glass. Good sensitivity to gas phase carbon dioxide was observed in the 0–20% range, with rapid response. A solid-state optical sensor device is described which could lead to thin film waveguide sensors suitable for mass production.

Introduction

The design of optical chemical sensors for the detection of carbon dioxide gas is normally based upon the interrogation of either a fluorescent or colorimetric pH indicator dye. Such devices are intrinsically responsive to pH variations in the local atmosphere and can be utilised for the detection of carbon dioxide in environments where possible interference from other acidic or basic species is negligible. Applications such as the determination of dissolved carbon dioxide and respiratory gas analysis have been identified for this type of sensor, where detection limit and moisture insensitivity requirements are less demanding than for other areas where alternative carbon dioxide analysis techniques would be required.

The pH-sensitive fluorescent dye 1-hydroxypyrene-3,6,8-tri-sulfonate (pyranine) shows absorption and emission bands in the visible region, and has been exploited in many previously described aqueous-phase carbon dioxide optical sensor devices.[1–8] Pyranine displays an absorption band associated with the deprotonated dye in the blue region of the spectrum, which is emissive in the green upon excitation. Gaseous carbon dioxide dissolves in water contained within a hydrous sensor membrane to form carbonic acid, which interacts with the deprotonated dye and results in a decrease of the green fluorescence. The use of polar dyes places an important restriction upon the range of matrices that can be used for immobilisation. The support material has to display good solubility towards the dye and must also retain sufficient moisture to facilitate the water-mediated sensor chemistry. If the sensor membrane should dry out it will no longer be responsive to CO_2.

For liquid phase CO_2 detection the classical device requires a buffered, dye-doped layer of hydrophilic support material, such as a hydrogel[1] or moisture-rich sol–gel glass,[8] to be maintained beneath a hydrophobic gas-permeable membrane, such as Teflon. The buffer ensures that the dye is deprotonated in the initial state and the hydrophobic membrane prevents liquid from entering or escaping from the dye-doped layer. However, the application of this configuration to gas phase sensing is limited by the need to maintain the moisture level in the sensitive membrane, as the application of dry gas will quickly render such sensor layers useless.

Recently, Mills *et al.*[9–14] and Weigl and Wolfbeis[15,16] have reported a means of overcoming the need for a moisture-rich environment. They have employed an ion-pair approach to encapsulate highly polar, pH-dependent dyes into hydrophobic materials such as ethylcellulose and silicone rubber. This methodology employs a phase transfer reagent to incorporate the polar dye in the lipophilic support matrix. It is proposed that during this incorporation procedure there is a significant quantity of moisture, in the form of water of crystallisation, encapsulated in the immobilisation matrix along with the dye.[9]

We have immobilised pyranine in a hydrophobic sol–gel derived glass by the use of a phase transfer reagent, creating a lipophilic dye–counter-ion pair that allows the polar dye to be incorporated in the organically modified silica (ormosil) glass. The glass matrix offers a highly stable microporous environment that can be easily deposited on a suitable substrate by means of dip coating. Moreover, these materials offer the sensitivity and rapid response of the polymer films described by other workers,[9–16] with the added ease of preparation, robustness, stability and uniformity of sol–gel derived glass thin films.

The sol–gel process [17,18] can be used to produce porous glass films in which sensor dyes can be entrapped. With a careful choice of precursor, ormosil glass can be produced with a pronounced hydrophobicity and a reduced amount of physisorbed and chemisorbed water in the matrix.[19–21] This offers a simple and effective room temperature route to producing glass, in which encapsulation of dye material occurs on the catalytic hydrolysis of the precursor, and subsequent condensation, resulting in the formation of microporous networks.[17,18,22–24] The partial hydrolysis of silica alkoxides such as tetraethyl orthosilicate (TEOS), as employed for pyranine immobilisation in previous studies,[6,8] results in the retention of a proportion of Si–OH linkages on the surface of the pores. These silanol groups have a pronounced effect on the state of the fluorophore within the matrix. Interaction of the dye with silanol groups within the glass will effectively protonate the dye and render it insensitive to the analyte,[25] unless an aqueous buffered layer is maintained. In ormosil glass precursors one of the alkoxy groups is replaced by an unreactive alkyl group, the nature of which greatly influences the characteristics of the final glass. These alkyl groups, which remain unchanged during the preparation of the sol–gel, align in the terminal position on formation of the xerogel network. The dissociation equilibrium of pyranine is highly dependent on the surrounding environment during the gel–xerogel transition[26,27] and, as the surface of the pore now has a large population of alkyl groups that do not interact readily with the protonated dye, the fluorescence emission at 515 nm associated with the deprotonated state

becomes more prominent.[28] The deprotonated form of the dye is also more stable within water rich environments, as the proton acceptor capabilities of water allow the deprotonated dye to dominate. In solvents with low proton acceptor capabilities, such as ethanol, the protonated dye will prevail.

We are able to incorporate the deprotonated form of pyranine into an ormosil-derived glass by the use of a phase transfer reagent. The alkyl chains in the counter-ion interact with those in the ormosil upon formation of the xerogel, and the deprotonated form of the dye can now exist within the lipophilic network. Elsewhere, a fluorescent pH dye has been entrapped in a mixed ormosil–silica glass matrix.[29] However, no attempt to modify the dye was made, and consequently the sensor performance was shown to be poor in comparison with the dye immobilised in moisture-rich silica glass. In particular, the great disadvantage of the TEOS-derived matrix is that colorimetric sensors produced using this support material have been shown to have very long response times.[25] In such cases, the speed of the sensor chemistry is kinetically driven by a combination of the dissociation equilibrium of the indicator and the interaction of the analyte gas with water bound within the matrix. These processes are slow compared with the diffusion of gas through the sensing membrane, as both the indicator and water have an intrinsic affinity for the polar silanol groups that are available within the TEOS glass matrix. On employing a lipophilic glass, we can eliminate these interactions and the sensor chemistry becomes diffusion controlled, and therefore faster.

The sensing process can be described in terms of the equation

$$QD \cdot xH_2O + CO_2 \rightleftharpoons QHCO_3 + HD \cdot (x-1)H_2O \qquad (1)$$
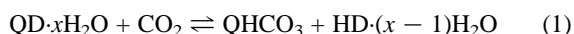
where Q is the counter ion and D the pyranine dye. We assume here that further protonation of the tribasic dye provides a negligible contribution to the overall fluorescence intensity. From this equation the following expression can be derived:[11]

$$K\alpha = (I^0 - I)/I \qquad (2)$$

where K is the equilibrium constant of eqn. (1), α is the percentage of carbon dioxide in the gas mixture, I^0 is the fluorescence intensity under nitrogen and I is the fluorescence intensity for a given α. All fluorescence from the protonated dye is excluded by optical filter selection, and hence is not considered in eqn. (2).

Experimental

Materials

1-Hydroxypyrene-3,6,8-trisulfonate was purchased from Kodak (Rochester, NY, USA) and used without further purification. Methyltriethoxysilane (MTEOS), ethyltriethoxysilane (ETEOS), tetraoctylammonium bromide and silver oxide were purchased from Aldrich (Gillingham, UK). De-ionised water was used throughout.

Apparatus

Fluorescence measurements were undertaken using the characterisation system shown in Fig. 1. Slides coated with the doped ormosil glass were held firmly in place and illuminated by a blue light emitting diode (λ_{max} = 450 nm) coupled with a 430 nm interference filter (bandwidth 10 nm) and a lens. The emitted light was collected at 90° to the excitation beam and focused by a lens through a high-pass filter (λ_{cut-on} 495 nm) on to the detector. Dedicated lock-in detection circuitry, which was used to control the LED and photodiode, has been described in

detail elsewhere.[30] The gas flow was regulated by the use of mass flow controllers (Unit Instruments, Dublin, Ireland) with a constant total flow rate of 500 cm^3 min^{-1}. Control of the moisture content of the nitrogen carrier gas was achieved by dividing the nitrogen stream into two parts before mixing with the analyte gas. A humidified component (achieved by bubbling through water) and a dry component were mixed together to obtain gas of the required relative humidity, which was monitored by a relative humidity meter (TH210, Eirelec, Dundalk, Ireland) before delivery to the flow cell. Unless stated otherwise, the relative humidity of the gas mixtures used in this study was maintained at 80%.

Thin film deposition

Sol–gel derived glass films were fabricated on clean soda-glass slides (Blue Star, Smethwick, UK). A dip coating procedure was used to achieve films of thickness that can be controlled by parameters such as solution viscosity and dip speed.[22,31–33] Film thickness was measured on glass and corroborated on silicon wafer by a combination of ellipsometry (Rudolph Research AutoELIII) and transmission spectroscopy[34] (Shimadzu UV-1201).

Preparation of dye-doped glass coatings

Tetraoctylammonium hydroxide (TOAOH) solution was prepared by stirring silver oxide (0.58 g, 2.5 mM) and tetra-octylammonium bromide (1.4 g, 2.5 mM) in methanol (10 ml) for 4 h. The methanolic free base was decanted and stored in a refrigerator.

Tetraoctylammonium bromide (0.6 g, 1.1 mM) was dissolved in 10 g of either methyltriethoxysilane or ethyltriethoxysilane with the addition of a few drops of dichloromethane. This was added to pyranine (0.2 g, 0.38 mM) in aqueous NaOH (0.1 M, 20 ml) and stirred. The organic layer was extracted and washed several times with water. This solution of the ion pair in ormosil (MTEOS 4.0 g, ETEOS 4.4 g) was added dropwise to aqueous HCl at pH 2 (1.6 g) and stirred for 1 h. Various amounts of tetraoctylammonium hydroxide solution were added before slides were dip-coated to produce films of thickness 650 nm, 1.2 µm and 1.7 µm. The samples were dried at 70 °C overnight and then left to stabilise in ambient conditions for 1 week prior to examination.
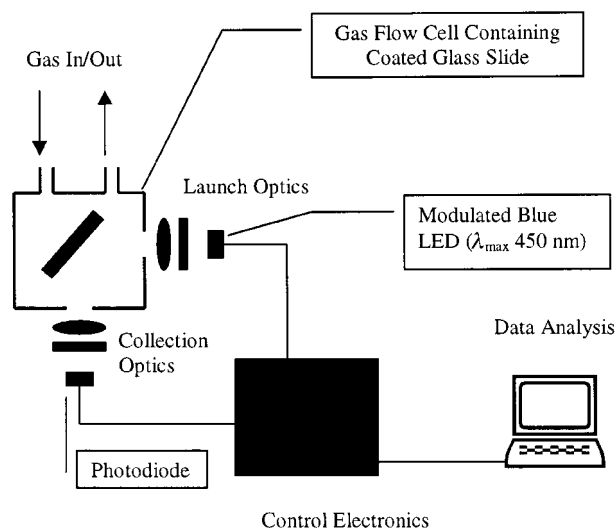

Fig. 1 Schematic diagram of the fluorescence sensing apparatus.

Results and discussion

A range of ormosil-derived glass thin films incorporating the fluorescent dye pyranine was produced. This pH sensitive material exhibits excitation peaks at 390 and 440 nm for its protonated and deprotonated forms, respectively. Illumination at these wavelengths results in emission at 450 nm for the former and 515 nm for the latter. By using suitable filters we can minimise any contributions from the protonated form of the dye and concentrate fully on the light emitted by the deprotonated species.

Films of pyranine entrapped in MTEOS- and ETEOS-derived glass of varyious thicknesses were fabricated, with the addition of increasing amounts of TOAOH solution. In the absence of the addition of free base it was found that the blue emission from the protonated form of the dye dominated, which may be a result of the formation of ethanol as a by-product during the sol–gel process. Films prepared from this solution yielded no sensitivity to carbon dioxide. However, on addition of a small amount of the methanolic solution of TOAOH, bright green fluorescence was observed, and the samples were responsive on exposure to the analyte gas. For an ETEOS film of thickness 1.7 μm with 0.8 ml of TOAOH solution, the response to CO_2 shown in Fig. 2 was obtained. The use of MTEOS in preparing the ormosil-derived thin films was also investigated and similar characteristics were displayed by these samples compared with ETEOS-derived glass films.

The thickness of the coating was found to have a pronounced effect on film sensitivity, as displayed in Fig. 3. The comparative term $(I^0 - I)/I^0$ used in this instance is derived from the change in fluorescence intensity $(I^0 - I)$ on exposure to CO_2, with reference to the fluorescence intensity under nitrogen (I^0). Here we find that the sensor response increases with film thickness. The effect of increasing amounts of added free base is also illustrated in Fig. 3, and it can be seen that the addition of TOA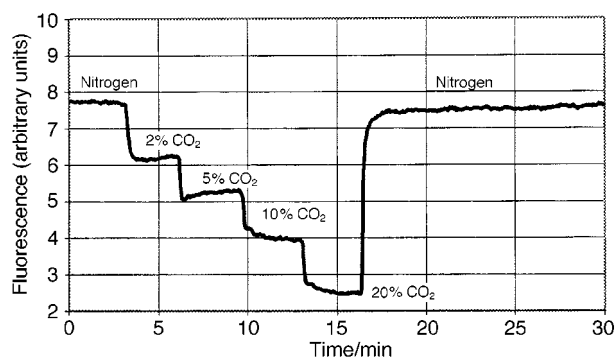OH has a very pronounced effect of the sensitivity towards the analyte, as a result of its influence on the dissociation equilibrium of the dye.

The limit of detection[35] for both of these samples was found to be below 0.1% CO_2, the MTEOS-derived film showing slightly better sensitivity than the ETEOS-derived film. The response times (the time to achieve 90% of the overall signal change), $\downarrow T_{90}$, and recovery times, $\uparrow T_{90}$, on exposure to 2% CO_2 for both ETEOS and MTEOS films of thickness 1.7 μm were in the region of 30 s. These times indicate that the sensing process is controlled by the diffusion of analyte gas through the sensing membrane, as opposed to being kinetically controlled. There is, however, a large contribution to these times from the volume of the flow cell. The apparatus used here was for characterisation purposes only, and a significantly lower flow cell volume is required for evaluation of the true response time. We have recently reported a compact fluorescence capture sensing design,[36] the application of which to carbon dioxide sensing is in progress, and this may reveal substantially quicker response times for these films. As response times have been reported to be less than 10 s for thick polymeric films,[11] and the diffusion of gas through thin, porous ormosil films is a fast process, we would expect our ormosil derived films to display response times of this order. In this study, however, it is evident that we are observing the extent of gas mixing in the flow system.

A plot of $(I^0 - I)/I$ against the percentage of carbon dioxide in the gas mixture is shown in Fig. 4 for ormosil (ETEOS and MTEOS) dye-doped films of thickness 1.7 μm with 0.8 ml of added base. Linear fits were obtained for both sets of data, the gradients of which (0.11 and 0.17 for ETEOS and MTEOS films, respectively) represent the equilibrium constant K of the dye in the sensor membrane. These values indicate the comparable sensitivities of the films, the variation in which may be accounted for by microstructural differences in the ormosil matrices. Correlation coefficients for the linear fits of 0.975 (MTEOS) and 0.996 (ETEOS) reflect an increased signal stability encountered with dye-doped membranes fabricated using the ormosil precursor with the longer alkyl chain length, although these were found to have slightly reduced sensitivity, reflected in the value of K.

Moisture sensitivity

The influence of humidity on the fluorescence of a dye-doped ormosil glass film under a nitrogen gas atmosphere was also investigated. This showed an increase in intensity proportional to relative humidity over the full range. This indicates that the film is significantly permeable to water vapour (as opposed to liquid water, the penetration of which through an ormosil-derived glass matrix is severely restricted[37]), as is also the case for hydrophobic polymers such as silicone rubber. As a result of

Fig. 2 Response of ETEOS-derived pyranine-doped film of thickness 1.7 μm with 0.8 ml of added TOAOH to various concentrations of CO_2.

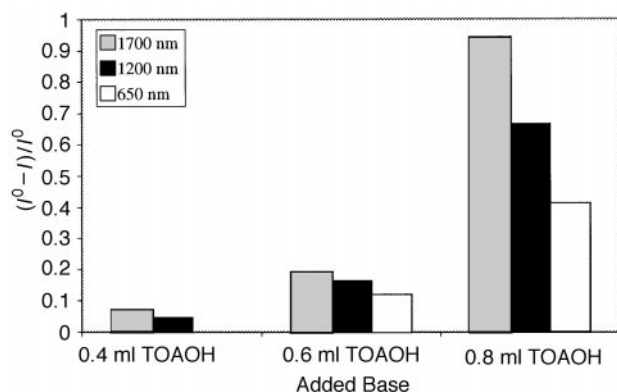**Fig. 3** Variation in signal response towards 20% CO_2 with film thickness and amount of added base for MTEOS-derived pyranine doped films.
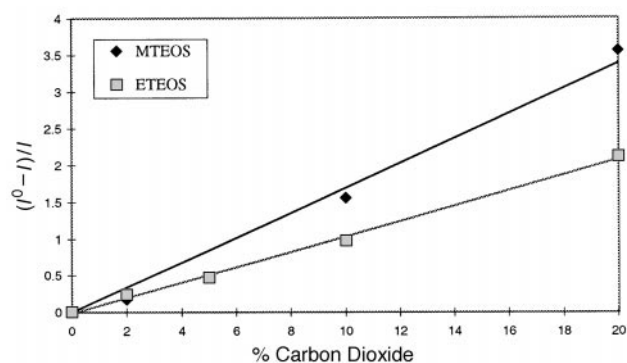

Fig. 4 Plot of $(I^0 - I)/I$ against CO_2 concentration for ormosil dye-doped films of thickness 1.7 μm with 0.8 ml of added TOAOH.

this permeation, the environment of the immobilised dye changes with the moisture content of the gas atmosphere, as reflected in the observed emission intensity changes. Such behaviour indicates that the sensor might best be employed in an atmosphere of fixed relative humidity, such as is encountered in respiratory gas analysis.

There is, however, still good, reversible sensor response towards CO_2 at 0% humidity, indicating that there is still sufficient moisture (as water of crystallisation of the ion pair) within the film to facilitate a response to the analyte gas. This behaviour is found to be highly reproducible, and no irreversible dehydration of the sensor membrane is observed on exposure to dry gas.

Stability of sensor membranes

In entrapping the dye material in ormosil-derived glass films we have succeeded in eliminating several factors that could affect the fluorescence of pyranine when immobilised in hydrophilic glass or polymeric films. The ormosil glass network is relatively uniform in nature and has been shown to be highly stable, undergoing no further evolution after the gel–xerogel transition and drying stages. Therefore, this material is not prone to any further evolution, deactivation through heat treatment or drying, or attack by plasticiser, as is the case for polymeric films.[15] These films also maintain their sensitivity to CO_2 for as long as 6 months when stored in ambient conditions. Eventual degradation of the performance of these sensitive films is attributed to the dehydration of the counter ion with time, rather than any change in the sol–gel matrix.

Conclusions

We have successfully employed a phase transfer reagent to incorporate the fluorescent dye pyranine into ormosil-derived glass thin films. Good sensitivity is displayed over a wide range of CO_2 concentrations, with response and recovery times of less than 1 min. The use of an ormosil sol–gel glass support matrix gives these films distinct advantages over previously reported pyranine-doped glass films, providing a simple route for the production of robust and stable hydrophobic thin films of a well defined thickness and excellent gas permeability characteristics that are comparatively uniform in nature and which could be employed in a planar waveguide fluorescence capture configuration. The stability of the dye-doped films was found to be good, even with storage in ambient conditions.

Acknowledgement

References

1 C. Munkholm, D. R. Walt and F. P. Milanovich, *Talanta*, 1988, **35**, 109.
2 B. Müller and P. C. Hauser, *Analyst*, 1996, **121**, 339.
3 J. Samuel, A. Strinkovski, K. Lieberman, M. Ottolenghi, D. Avnir and A. Lewis, *Mater. Lett.*, 1994, **21**, 431.
4 X. He and G. A. Rechnitz, *Anal. Chem.,* 1995, **67**, 2264.
5 O. S. Wolfbeis, L. J. Weis, M. J. Leiner and W. E. Ziegler, *Anal. Chem.,* 1988, **60**, 2028.
6 D. A. Nivens, M. V. Schiza and S. M. Angel, *Proc. SPIE,* 1997, **3105**, 52.
7 S. G. Schulman, S. Chen, F. Bai, M. J. P. Leiner, L. Weis and O. S. Wolfbeis, *Anal. Chim. Acta,* 1995, **304**, 165.
8 S. C. Kraus, R. Czolk, J. Reichert and H. J. Ache, *Sens. Actuators B*, 1993, **15–16**, 199.
9 A. Mills, Q. Chang and N. McMurray, *Anal. Chem.*, 1992, **64**, 1383.
10 A. Mills and Q. Chang, *Anal. Chim. Acta*, 1994, **285**, 113.
11 A. Mills and Q. Chang, *Analyst*, 1993, **118**, 839.
12 A. Mills and Q. Chang, *Sens. Actuators B*, 1994, **21**, 83.
13 A. Mills, A. Lepre and L. Wild, *Sens. Actuators B*, 1997, **38–39**, 419.
14 A. Mills and L. Monaf, *Analyst*, 1996, **121**, 535.
15 B. H. Weigl and O. S. Wolfbeis, *Anal. Chim. Acta,* 1995, **302**, 249.
16 B. H. Weigl and O. S. Wolfbeis, *Sens. Actuators B*, 1995, **28**, 151.
17 C. J. Brinker and G. W. Scherer, *Sol–Gel Science, the Physics and Chemistry of Sol–Gel Processing*, Academic Press, London, 1990.
18 *Better Ceramics Through Chemistry III*, ed. C. J. Brinker, D. E. Clark and D. R. Ulrich, Materials Research Society, Pittsburgh, PA, 1988.
19 J. Kron, S. Amberg-Schwab and G. Schottner, *J. Sol–Gel Sci. Technol.,* 1994, **2**, 189.
20 J. D. Mackenzie, *J. Sol–Gel Sci. Technol.,* 1994, **2**, 81.
21 P. Innocenzi, M. O. Abdirashid and M. Guglielmi, *J. Sol–Gel Sci. Technol.,* 1994, **3**, 189.
22 C. J. Brinker, A. J. Hurd, P. R. Schmuck, G. C. Frye and C. S. Ashley, *J. Non-Cryst. Solids*, 1992, **147**, 424.
23 C. M. McDonagh, F. Sheridan, T. Butler and B. D. MacCraith, *J. Non-Cryst. Solids*, 1996, **194**, 72.
24 B. D. MacCraith, C. M. McDonagh, G. O'Keeffe, A. K. McEvoy, T. Butler and F. Sheridan, *Sens. Actuators B*, 1995, **29**, 51.
25 J. Lin and C. W. Brown, *Trends Anal. Chem.,* 1997, **16**, 200, and references cited therein.
26 J. C. Pouxviel, B. Dunn and J. I. Zink, *J. Phys. Chem.*, 1989, **93**, 2134.
27 F. Nishida, B. Dunn, J. M. McKiernan, J. I. Zink, C. J. Brinker and A. J. Hurd, *J. Sol–Gel Sci. Technol.,* 1994, **2**, 477.
28 N. Wittouck, F. De Schryver and I. Snijkers-Hendrickx, *J. Sol–Gel Sci. Tech.*, 1997, **8**, 895.
29 A. Lobnik, I. Oehme, I. Murkovic and O. S. Wolfbeis, *Anal. Chim. Acta*, 1998, **367**, 159.
30 P. C. Hauser and S. S. Tan, *Analyst*, 1993, **118**, 991.
31 I. M. Thomas, in *Sol–Gel Optics: Processing and Applications*, ed. L. C. Klein, Kluwer, Dordrecht, 1994, p. 141.
32 L. E. Scriven, in *Better Ceramics Through Chemistry III*, ed. C. J. Brinker, D. E. Clark and D. R. Ulrich, Materials Research Society, Pittsburgh, PA, 1988, p. 717.
33 I. Strawbridge and P. F. James, *J. Non-Cryst. Solids,* 1986, **86**, 381.
34 F. Regan, B. D. MacCraith, J. E. Walsh, K. O'Dwyer, J. G. Vos and M. Meaney, *Vibr. Spectrosc.,* 1997, **14**, 239.
35 J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, Ellis Horwood, Chichester, 1988, p. 115.
36 J.-F. Gouin, A. Doyle and B. D. MacCraith, *Electron. Lett.*, 1998, **34**, 1685.
37 P. Lavin, MSc Thesis, Dublin City University, 1997.

Paper 8/05803B