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Nitrogen dioxide sensing characteristics at elevated temperature of sol–gel glass thin films containing substituted porphyrin dyes

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An optical gas sensor device based on tetra-substituted porphyrin dye entrapped in sol–gel glass displays greatly improved signal strength (1400% at 295 K) on exposure to 4.4 ppm nitrogen dioxide (in N_2) gas compared to a multilayer Langmuir–Blodgett film fabricated from the same porphyrin. Temporal response was found to be similar, but differences in the two deposition methods were observed in terms of signal strength and response/recovery times. This behaviour is explained in terms of the differing nature of the two film types. A room temperature sensitivity of 176 ppb was measured and the response obeyed Langmuir adsorption kinetics.

1. Introduction

Over a number of years there has been a large volume of literature concerning dedicated gas sensor devices for laboratory and industrial applications. Areas that best highlight this include the environmental monitoring of toxic gases, development of emergency early-warning systems and the possibility of *in vivo* monitoring of blood gases.[1] With respect to nitrogen dioxide gas sensing, a number of detection techniques have been discussed in the literature, including conductometric[2] and micro-gravimetric methods,[3] and more recently work by ourselves and others monitoring changes in the optical properties of thin films in the presence of analyte gas.[4] An excellent review of the major principles of optical sensor design and application and discussion of the numerous advantages of this approach over more well established methods can be found elsewhere,[5] but principally these are the low power requirement, low cost and electrical isolation possible with optical sensor systems.

Several types of material have been reported as displaying spectral modulation in the presence of nitrogen dioxide, and have subsequently been incorporated into optical sensor devices. These include metal oxides,[6] polymers,[7] phthalocyanines,[8] azobenzenes[9] and porphyrins.[10] Porphyrins are highly conjugated organic molecules which have been used for a number of sensor applications[11] due to their inherent chemical stability and favourable optical properties including spectral changes in the visible region (400–900 nm) which will enable the use of cheap LED's in a commercial device.

The ideal sensor operates over a range of temperatures with no discernible loss of response, is highly selective and exhibits fast temporal response and recovery characteristics.[12] While many devices have been previously detailed, operation in environments of elevated temperature is rarely reported, mainly due to the fact that very often sensor performance beyond ambient laboratory conditions is disappointing. In this paper we aim to highlight the sensing characteristics of our laboratory prototype at elevated temperatures that are often found in industrial environments.

When considering thin film sensors, a high surface area to volume ratio of the chemical transducer is desirable for optimum gas sensing performance. A variety of thin film deposition techniques have been utilised to this end, such as vacuum evaporation[13] and spin-coating.[14] Deposition of thin films using the Langmuir–Blodgett (LB) technique has led to excellent gas sensing response for a number of organic compounds.[15] However, LB films of porphyrins are well known to have poor stability with respect to mechanical and thermal treatment[16] and entrapment of organics in a sol–gel matrix has been shown to stabilise the film for other systems.[17] A further disadvantage of using LB films for gas sensing is the labour intensive nature of the film fabrication, which requires specialised equipment for the deposition of films of reproducibly high quality.

The sol–gel process is an ambient temperature method that may be used to fabricate thin glass films that have well defined optical and physical characteristics, such as thickness, porosity and refractive index. Details of the influence of varying process parameters on the properties of the resultant silica films are described elsewhere,[18,19] but in general, factors such as pH and ratio of water to silicone alkoxide precursor can be used to define the nature of the glass. Analyte-sensitive reagents may be added at the precursor stage, and will subsequently become entrapped in the porous coating to yield dye-doped sensor films. Sol–gel-derived materials have been used in the development of a wide range of optical sensors for pH monitoring[20] and the detection of analytes such as dissolved oxygen[21] and ammonia gas.[22,23] We have entrapped the porphyrin dye within sol–gel glass films fabricated from a methyltriethoxysilane (MTEOS) precursor. The substitution of a reactive alkoxy group in the glass precursor with an unreactive alkyl group results in decreased polarity and hydrophilicity of the resulting organically modified silica (ormosil) glass surface.[24,25] These alkyl functions populate the surface of the micro-porous glass, thereby reducing the tendency of films prepared under conditions of acid catalysis to be significantly acidic and hydrophilic. Such characteristics make these films ideal hosts for the type of porphyrin dye materials we have employed during this study, which are not readily compatible with hydrous environments.

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One of the aims of this work was to show that the entrapment of the porphyrin in a sol–gel matrix could produce a film with gas sensing characteristics comparable to the much thinner LB film analogue. The highly micro-porous nature of sol–gel derived glass thin films facilitates gaseous flow, but in general thin films mechanically deposited onto glass or polymeric substrates are an order of magnitude thicker than a multilayer LB film. Previous work has shown that entrapment of an azobenzene derivative in a sol–gel matrix enabled fast and sensitive response to NO_2 gas,[26,27] that showed often superior sensor performance in comparison to the LB film analogue, and we aim to further illustrate this using our own sensor system.

2. Experimental

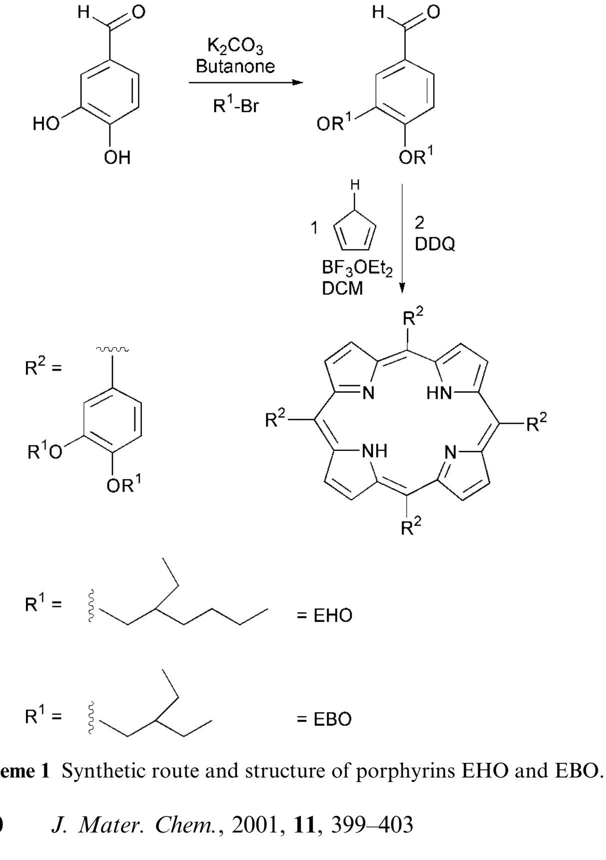
2.1. Materials

The synthesis and structures of the dye materials 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21*H*,23*H*-porphine (EHO) and 5,10,15,20-tetrakis[3,4-bis(2-ethylbutoxy)phenyl]-21*H*,23*H*-porphine (EBO) are shown in Scheme 1. The synthesis and characterisation of EHO is described elsewhere.[28] Similar procedures were used in the synthesis of EBO and characterised as follows.

^{1}H NMR 250 MHz ($CDCl_3$): δ (ppm) = 8.823 (s, 8H), 7.785 (s, 4H), 7.711 (d, 4H, $^3J_{HH} = 8.2$ Hz), 7.244 (d, 4H, $^3J_{HH} = 8.2$ Hz), 4.184 (d, 8H, $^3J_{HH} = 5.8$ Hz), 4.095 (d, 8H, $^3J_{HH} = 5.8$ Hz), 1.908 (q, 4H, $^3J_{HH} = 5.8$ Hz), 1.85–1.42 (m, 36 H), 1.076 (t, 24H, $^3J_{HH} = 7.4$ Hz), 0.923 (t, 24H, $^3J_{HH} = 7.4$ Hz), −2.738 (s, 2H). UV–VIS ($CHCl_3$): λ_{max}/nm ($\varepsilon \times 10^{-3}$ mol^{-1} l cm^{-1}) = 427 (408), 521 (19), 557 (12), 594 (7), 650 (6). FAB (+ve), *m*/*z*: 1414 (M^+) (Calc. for $C_{92}H_{126}O_8$ 1414). Melting point: 250–253 °C.

2.2. Langmuir–Blodgett film deposition

Thin film assemblies of EHO were prepared using a constant perimeter Joyce–Loebl mini-trough. The porphyrin solution was spread onto a pure water subphase (pH ≈ 6.2, 20 °C) and transferred using a fast-deposition technique onto glass plates (rendered hydrophobic by immersion in 1,1,1,3,3,3-hexamethyldisilazane (HMDS) for 24 h) at a rate of 1000 mm min^{-1} and a surface pressure of 15 mN m^{-1}. The transfer rate was much greater than for conventional LB film deposition.



Scheme 1 Synthetic route and structure of porphyrins EHO and EBO.

2.3. Deposition of sol–gel thin films

Porphyrin dye (EBO or EHO, 5 mg) was completely dissolved in MTEOS (1.60 g) by the addition of 2–3 drops of chloroform. The resultant deep purple solution was then vigorously stirred during the dropwise addition of aqueous HCl (pH 1, 0.42 g). Stirring was continued for one hour, after which the solution had become homogeneous and had developed a dark green colour. This sol was immediately used to spin coat thin films of porphyrin doped sol–gel onto glass substrates.

A few drops of the dye-doped sol were placed onto the surface of clean glass slides (Blue Star, Smethwick, UK), revolving at 6000 rpm. These produced consistent films of a thickness of approximately 500 nm. The coated glass slides were dried overnight (70 °C), and were left to stabilise in laboratory conditions for one week to ensure that any post-fabrication structural evolution of the glass films that may affect the porosity and thickness had gone to completion.[19]

2.4. Gas sensing

The NO_2 sensing chamber was designed in-house[29] and is shown in Fig. 1. Absorbance changes were monitored using a World Precision Instruments optical fibre spectrophotometer driven by Spectromate software. Thermostatic control of the sensor films involved fixing the substrate in position together with a Peltier heater/cooling system and passing the gas in a direction perpendicular to the light interrogation. Nitrogen dioxide (4.4 ppm in nitrogen, BOC, Guilford, UK) was flowed through the gas chamber *via* the minimum length of Teflon tubing. The response temperature of each exposure was varied and is shown on the relevant diagrams. The temperature of recovery in nitrogen (BOC, Guildford, UK) was fixed at 353 K for all experiments. Elevated temperatures were used in the recovery cycles due to the slow (several hours) recovery observed at room temperature for these systems.

The signal strength of the gas response was calculated using eqn. (1),

$$S_\lambda = \left| \frac{A_o - A_t}{A_o} \right| \times 100 \qquad (1)$$

where S_λ = the signal strength at a given wavelength; A_t = the absorbance after exposure to gas at equilibrium; A_0 = the absorbance before exposure to gas.

2.5 Adsorption/desorption theory

There are a number of isotherm models which describe the adsorption/desorption of gas molecules onto a solid surface including the BET,[30] Toth,[31] Freundlich[32] and Hill[33] models amongst others. A review of these is provided elsewhere.[34] The

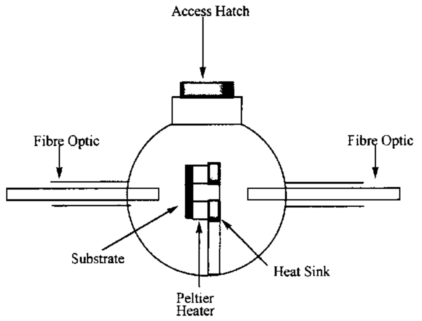


Fig. 1 Schematic design of sensing apparatus. Gas flow direction is perpendicular to the substrate.

simplest isotherm model to describe the adsorption of a gas onto a solid surface (and the model on which a number of the subsequent isotherms above were based) is the Langmuir adsorption isotherm[35] which has been used by a number of workers to characterise their systems.[36] The Langmuir adsorption isotherm is usually expressed as eqn. (2),

$$\theta = \left(\frac{n_{\mathrm{ads}}}{N_{\mathrm{s}}}\right) = \left[\frac{\lambda c}{1+\lambda c}\right] \qquad (2)$$

where θ = fractional surface coverage; n_{ads} = number of molecules of gas adsorbed ($\propto$ ΔAbsorbance.); N_{s} = number of adsorption sites; λ = constant relating to the adsorbability of the gas; c = concentration of the gas.

By rearranging eqn. (2) the following relationship [eqn. (3)] is obtained.

$$\left(\frac{c}{n_{\mathrm{ads}}}\right) = \left(\frac{c}{N_{\mathrm{s}}}\right) + \left(\frac{1}{N_{\mathrm{s}}\lambda}\right) \qquad (3)$$

Therefore a plot of c/n_{ads} *vs.* c will be a straight line if Langmuir kinetics are obeyed.

3. Results and discussion

We succeeded in entrapping two similar substituted porphyrin dyes in both LB films and within a sol–gel matrix. The acidic preparative conditions involved in sol–gel synthesis proved non-detrimental to the dye materials despite the colour change from violet to green in the evolving sol. The colour change is probably related to incomplete hydrolysis and condensation within the sol. These groups are capable of interacting with electron rich species such as the porphyrin dye, and in doing so will effect the above colour change.[37] However these interactions are not strong enough to prevent the analyte interacting with the dye and the desired sensor response being resultant.[38]

The UV–Visible absorption spectrum of an EHO–MTEOS thin film, under a nitrogen atmosphere, shows the characteristic Soret band at 430 nm with Q-bands at 480, 500 and 520 nm, which are clearly displayed in Fig. 2. Both the spectra and subsequent variations on exposure to analyte gas are comparable for both LB film and sol–gel systems. On exposure to 4.4 ppm NO_2 at 293 K the absorption spectrum of the doped sol–gel film undergoes a significant hyperchromic shift at 470 nm and 700 nm with a simultaneous hypochromic shift of the Soret band at 435 nm. There also appears to be a small bathochromic shift ($\sim$5 nm) of the Soret peak which could be attributed to a change in the J-aggregation state of the porphyrins as observed in other organic systems.[39,40] It was found that while films of EBO–MTEOS displayed good absorption spectra, there was no observable change on exposure to 4.4 ppm NO_2. Only a small and slow response to NO_2 was observed when depositing the EBO material as a multilayer LB film. The NO_2 sensing behaviour of the EHO LB films is discussed in greater detail elsewhere,[28] but is similar to that described by the dye-doped sol–gel film. These films displayed fast response with high signal strength on exposure to 4.4 ppm NO_2, detailed in Table 1, which also outlines the NO_2 sensing characteristics of sol–gel entrapped dyes.

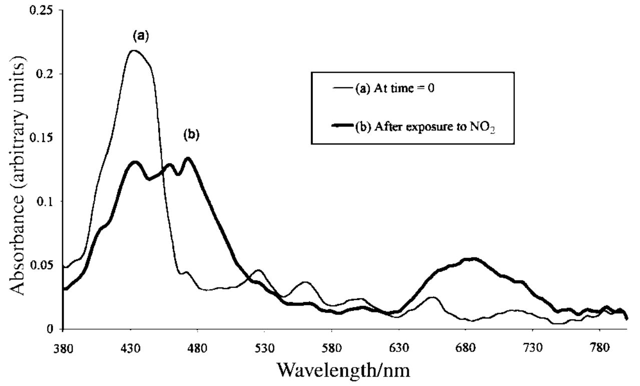


Fig. 2 UV–Visible absorption spectrum of EHO–MTEOS film before and after exposure to 4.4 ppm NO_2 at 295 K.

The response time data shown in Table 1 indicate that the sol–gel entrapped porphyrin film has faster temporal response during the fourth exposure to 4.4 ppm NO_2 compared to the first exposure. This pre-gassing phenomenon is common with diffusion-limited systems and has been attributed to the incomplete recovery of the system where the remaining adsorbed NO_2 molecules lower the required binding energy of NO_2 at the unoccupied sites on further exposures thus decreasing the response times.[41] A fast t_{50} response time is recorded for the LB film with a t_{90} response time approximately the same as the sol–gel film. This indicates that the significantly thinner LB film has a very fast initial reaction mechanism with the analyte gas (compared with the sol–gel), followed by a second slower mechanism obtaining full response. There is little significant change in the response kinetics of the LB films on multiple exposures.[28] This is probably because the LB system contains a very thin sensor layer and therefore diffusion related factors are less dominant.

A signal strength of approximately 1400% (at 470 nm) was observed for the EHO–MTEOS film, which is more than three times that observed for the multilayer LB film. However there is significant similarity in the signal strength of the two systems at the Soret peak and 700 nm. The response times of the sol–gel system are higher than the LB analogue implying that diffusion of the gas through the film is the limiting factor during the gas response for the sol–gel deposited thin films. A similar increase in the recovery times of the sol–gel compared with the LB film analogue would indicate that diffusion is also dominant during the recovery cycle. The classical numerical method for determining the effect of diffusion is to plot the change in absorbance as a function of the square root of time. However this equation could not be applied to our system and more complicated models based on the diffusion of gases at a heterogeneous surface are being investigated.

Fig. 3 shows the effect of temperature on gas sensing response at 470 nm for a EHO–MTEOS film on exposure to 4.4 ppm NO_2. A marked decrease in the response is observed as the temperature increases probably due to a shift in the equilibrium to desorption at elevated temperatures. As the temperature increases, the response times (t_{50} and t_{90}) decrease substantially until a loss of response above 350 K whereas the LB film did not demonstrate this significant loss of response despite heating to 373 K as shown in Table 2.

The fundamental differences in these two types of membrane are highlighted by this behaviour. The LB film system has a wider operating range with regard to temperature, and some response is shown even above 350 K. However, sol–gel films fail badly under these conditions due to their hydrous nature. It is clear that as the temperature of the system approaches the boiling point of water there is a drastic retardation in performance, which does not correspond to any thermal decay of the dye material or membrane, as simply cooling the film will restore its efficacy. We must therefore associate this with loss of moisture at elevated temperature. Dye-doped sol–gel films have been described previously as being very effective moisture sensors,[42] although to a lesser extent when considering ormosil films such as those described here. A number of features concerning moisture dependent sensor performance have been outlined in work by the authors in which the moisture content of the analyte gas is controlled.[43] In changing temperature we also vary the moisture content of the vapour phase as the vapour pressure of water in the sensor membrane rises with temperature, and this perhaps accounts for the temporal variations in sensor performance.

The t_{50} response times of the sol–gel to NO_2 reach a constant

Table 1 Data based on absorbance changes at 700 nm, 470 nm and 430 nm respectively on exposure to 4.4 ppm NO_2 at 293 K where t_{50}, and t_{90} are the times taken for 50% and 90% of overall signal for response (resp) and recovery (rec) respectively. Recovery temperature for all experiments was 353 K

Material	t_{50resp}/s	t_{90resp}/s	$S_{700\ nm}$(%)	$S_{470\ nm}$(%)	$S_{430\ nm}$(%)	t_{50rec}/s	t_{90rec}/s
EHO–LB film[31]	25	190	742	337	60	33	73
MTEOS–EHO Run1	112	383	750	1400	61	66	159
MTEOS–EHO Run 4	100	225	760	1350	58	47	134

level of 45 s (Table 2) at 325 K, whereas the t_{90} response times continue to decrease above this temperature. This phenomenon is not fully understood but a possible explanation is that at low temperatures more than one mechanism (diffusion and surface adsorption) is controlling the response. At elevated temperatures a single mechanism (diffusion) would appear to control the response time.

Fig. 4 shows the effect of NO_2 concentration on the response characteristics for the sol–gel–EHO system. A response to a concentration as low as 0.176 ppm (176 ppb) was obtained at room temperature using our present system. Using eqn. 2 (linear form of the Langmuir adsorption isotherm) a plot of c/n_{ads} *vs.* c gave a straight line (Fig. 5) indicating that Langmuir adsorption kinetics were obeyed. From Fig. 5 the number of adsorption sites is calculated from 1/gradient = 0.11 k A^{-1} where k is a constant.

One possible gas sensing mechanism involves protonation of the porphyrin ring because nitrogen dioxide dissolves in water to yield a mixture of nitrous and nitric acid and this process occurs within the sol–gel membrane, as there will be both chemisorbed and physisorbed moisture within the membrane available for solvation. Subsequent acid attack of the amine functionalities within the porphyrin backbone may offer a significant contribution to the spectral variations encountered here, which lessens as the moisture within the sol–gel film decreases at elevated temperature. The protonation mechanism is further emphasised by the addition of trifluoroacetic acid (TFA) to a solution of EHO in $CHCl_3$ which, when interrogated using UV–Visible spectroscopy, recorded similar spectral changes (Fig. 6) to the EHO–NO_2 gas system. However, direct protonation of the porphyrin ring would involve the formation of covalent bonds. This would require other chemical agents (*i.e.* alkalis) to facilitate full recovery to the unprotonated form. The EHO–NO_2 system exhibits full recovery (< 50 s) when a small amount of energy (heating) is applied to the substrate. Full recovery, within 3 hours, was also observed when the gassed sample was exposed to the air at room temperature. Therefore, the probable mechanism involves the interaction of the electrophilic NO_2 gas with the same sites where protonation occurs to account for the similar spectral changes. The incoming NO_2 forms a charge-transfer type bond with the active porphyrin sites and with the application of heat full recovery occurs because of the low energy involved in the charge-transfer bond.

The sudden loss of response to NO_2 for the MTEOS–EHO system above 350 K and its greater sensitivity compared with the LB system would indicate that moisture and the hydro-

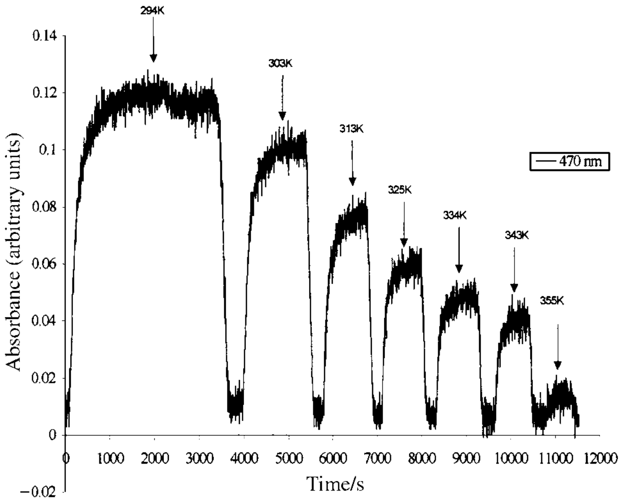


Fig. 3 Effect of temperature on absorption variation at 470 nm of EHO–MTEOS film on exposure to 4.4 ppm NO_2, recovery in N_2 at 353 K.

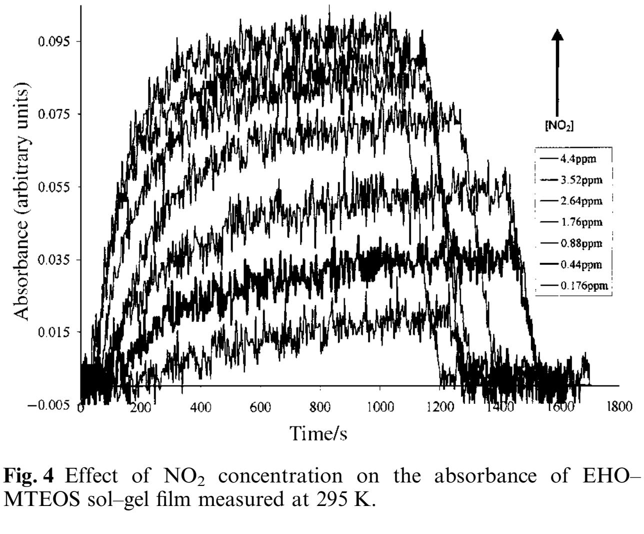


Fig. 4 Effect of NO_2 concentration on the absorbance of EHO–MTEOS sol–gel film measured at 295 K.

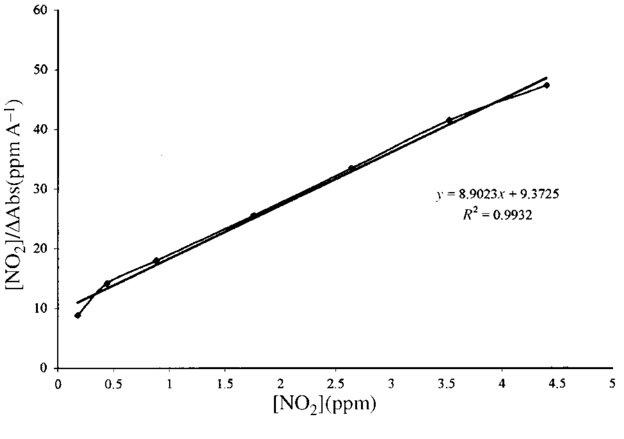


Fig. 5 Plot for linear form of the Langmuir adsorption isotherm for EHO–MTEOS sol–gel film.

Table 2 The effect of temperature on response times for EHO–MTEOS film on cyclic exposure to 4.4 ppm NO_2

T/K	t_{50resp}/s	t_{90resp}/s
294	112	383
303	84	285
313	55	262
325	44	212
334	45	199
343	45	167

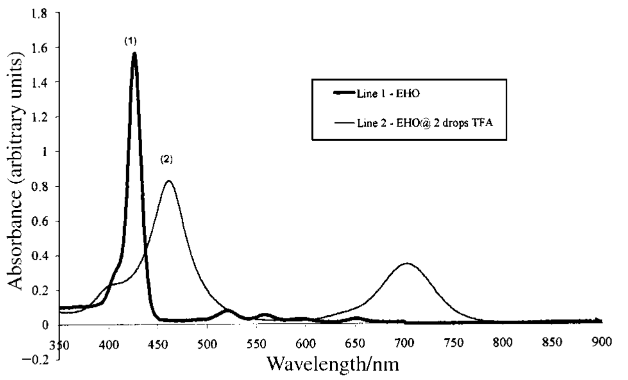


Fig. 6 UV–Visible absorbance spectrum detailing the effect of trifluoroacetic acid (TEA) on solution of EHO (unknown concentration) in $CHCl_3$.

philic nature of the sol–gel matrix are important for good gas sensing characteristics. However the exact effect of moisture on the gas sensing mechanism is not yet fully understood and is the subject of further work.

4. Conclusions

Sol–gel entrapped porphyrins were deposited as thin films and exposed to 4.4 ppm NO_2. Greater signal strength to the analyte gas compared with the LB film analogue indicates the possibility of using the more easily fabricated sol–gel thin film deposition method for producing organic gas sensors. A response to a concentration of NO_2 as low as 176 ppb was recorded at room temperature. A number of similarities are evident between the hydrous sol–gel films and the organic LB films, and there is evidence of strong moisture dependence of the sensor mechanism in dye-doped sol–gel films, which is not encountered for LB films.

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