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The use of thin silver films for the detection of low concentrations of hydrogen sulphide

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Abstract

This work describes the facile fabrication of a sensor for the visual detection of hydrogen sulphide at concentrations of $\geq$0.1 ppm. Colloidal silver films were prepared on PVC by a dip-coating method which, on exposure to hydrogen sulphide, underwent a colour change from yellow/grey to black. The rate of change was considerably faster than for films prepared by vacuum deposition. A visual change of the colloidal silver film was observed for hydrogen sulphide at 1 ppm within 10 min and at 0.1 ppm in 60 min. © 1998 Elsevier Science B.V.

1. Introduction

Various literature methods exist for colloidal silver preparation, including the reduction of silver nitrate using sodium citrate [1], ferrous citrate [2,3] or sodium borohydride [4–6] and the reduction of silver tartrate using ferrous tartrate [2]. Fabrication of silver films on frosted glass slides by the in situ formation of colloidal silver has also been reported [7]. We have utilised this latter method to produce films of various thicknesses for studies of the reaction between silver and hydrogen sulphide, which was monitored by measuring absorbance in the visible region.

Different methods have been developed for the detection of low concentrations of H_2S principally due to its high toxicity. Heated tin dioxide thin films have been used [8,9] and zinc oxide has been utilized for the measurement of volatile sulphur compounds in the breath [10]. Recently a gas sensor has been fabricated based on a tin dioxide/copper oxide mixture which showed a maximum in sensitivity and in selectivity at the relatively low operating temperature of 100°C [11]. An optical waveguide acid–vapour sensor has been shown to detect hydrogen sulphide although it is not specific for this gas and this is a serious drawback [12]. Fluorescence quenching has been demonstrated as a possible method for hydrogen sulphide sensing using thionine films [13] and fibre optic devices based on fluorescein mercuric sulphate [14]. This latter method involves conversion of hydrogen sulphide gas to the hydrosulphide ion prior to reaction with the dye.

Silver is known to react with a small number of gases only: for example hydrogen sulphide reacts with silver producing silver sulphide which is black. This process is mainly responsible for the tarnishing of silver metal in electrical connections, dentistry and jewellery. This phenomenon has been widely studied in order to prevent the deterioration of silver, but it has

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also been used to detect hydrogen sulphide gas at low concentrations (tens of ppm) by carrying out ellipsometry and conductivity measurements [15]. Porous silver electrodes have been also used for the detection of trace hydrogen sulphide (ppb levels) in gaseous samples [16].

Previous studies of the reaction of hydrogen sulphide with silver have been undertaken on bulk material or on relatively thick silver films [17]. This study involved the production of colloidal silver films in order to assess their ability to act as visual sensors for sulphur-containing compounds. Our study was initiated to investigate the fabrication of disposable sensors for hydrogen sulphide. Silver was selected for study due to the irreversible reaction with hydrogen sulphide which permits a cumulative response to the gas which is an advantage for some applications. As the reaction proceeds metallic reflectivity is decreased as the metal is converted to silver sulphide which absorbs in the visible range, thus permitting a visual cue to the presence of hydrogen sulphide. Our goal was a sensor which was capable of detecting low ppm levels of hydrogen sulphide.

2. Experimental

2.1. Materials

The water used to make all solutions was from a Purite filtration system and had a specific conductance of $<5\times10^{-5}$ mhos m^{-1} at 25°C. The materials used were as follows: silver nitrate, Aldrich (UK), 99+%; '880' ammonia solution, BDH (UK), AnalaR; sodium hydroxide, Fisons (UK) and D-glucose anhydrous, BDH (UK). All materials were used as received.

The various hydrogen sulphide gas cylinders (pure, 250 ppm, 10 ppm and 1 ppm) were obtained from BOC, Bristol.

2.2. Preparation of vacuum deposited silver films

Thin films of silver were produced by vacuum deposition using an Edwards Auto 306 vacuum coating unit, fitted with a 100 W, 13.56 MHz RF plasma generator. Microscope glass slides were used as substrates for the production of 25 nm thick silver films. The glass slides were cleaned with Decon, followed by nitric acid and then ethanol and dried overnight at 70°C.

2.3. Preparation of films by in situ formation of colloidal silver [7]

Tollen's reagent, which contains the $Ag(NH_3)_2^+$ complex, was reduced by glucose to form a silver film on various substrates introduced into the reaction mixture. These included glass slides (washed with concentrated nitric acid and rinsed with water), perspex and PVC. Tollen's reagent was prepared as follows: ca. 20 drops of a 5% w/v NaOH solution from a Pasteur pipette (ca. 0.6 cm^3) was added to 20 cm^3 of 2% w/v $AgNO_3$ solution in a small beaker. A mid-brown precipitate of AgOH was formed. This precipitate was re-dissolved by adding concentrated '880' ammonia solution (AnalaR) in a dropwise manner to form the soluble complex $Ag(NH_3)_2^+$. The mixture was cooled in an ice bath and then at t=0, 6 cm^3 of a 10% w/v solution of D-glucose was added and the glass slides were introduced into the mixture. Whilst in the ice bath the reaction mixture went through the following colour changes: slightly yellow (t=30 s), red (t=70 s) and then grey (t=100 s), indicating that colloidal silver was being formed and undergoing coagulation. The reaction mixture was then removed from the ice bath and allowed to reach room temperature; about 7 min after removal from the ice bath deposition of silver onto the glass slides had begun. The glass slides were removed at various times, rinsed with water and then air-dried. Slides removed between 16 and 25 min (after the reaction mixture had been removed from the ice bath) had a yellow/grey silver film on their surfaces.

In a separate experiment the adhesion and coherence of the film on various plastic substrates were investigated: a silver film was formed on perspex and PVC and the adhesion to PVC was superior to that on perspex. In another experiment strips of PVC were immersed into the reaction mixture and removed at various times: a film formed by t=21 min was not coherent, whilst films formed between t=28 and t=32 min were coherent and yellow/grey in transmission. By t=57 min a silver mirror had been formed on the substrate. (All times refer to the time elapsed after the removal of the reaction mixture from the ice-bath).

2.4. Reaction of colloidal silver with hydrogen sulphide

2.4.1. Preliminary comparison of the reactivity of vacuum deposited and colloidally produced silver films

A round-bottomed flask was flushed with pure, dry hydrogen sulphide and the silver films inserted into the flask which was then flushed again with hydrogen sulphide. The colour of the films was monitored visually with time.

2.4.2. Absorbance studies for the reaction of colloidal silver with dry hydrogen sulphide

For this experiment a constant flow of dry hydrogen sulphide (at various concentrations in nitrogen) over the sample was required in order to avoid any humidity effect on the reaction. A gas tight cell was designed by opening an inlet and an outlet in a polystyrene cell which were then connected to the gas cylinder and a trapping system consisting of a series of Dreschel bottles containing NaOCl. This gas-tight cell was glued to the cell holder in the spectrophotometer so that the sample would always be placed in the same position.

Three different concentrations of dry hydrogen sulphide were used (1 ppm, 10 ppm and 250 ppm) running spectra every 30 min for 150 min. The apparatus used was a Perkin-Elmer Lambda 15 UV–Vis Spectrophotometer in reflectance mode and the wavelength range was 400 to 800 nm.

2.4.3. Absorbance studies for the reaction of colloidal silver with hydrogen sulphide in laboratory air

A static method was employed for monitoring the absorbance changes of the colloidal silver thin films in contact with different concentrations of hydrogen sulphide in laboratory air. The samples were introduced into different flasks depending on the concentration of hydrogen sulphide required in each experiment and the hydrogen sulphide was injected into the flask using SGE 5 ml and 10 ml gas-tight syringes. The relative humidity of the laboratory air was either 46–49% or 61–63%. Absorbance measurements were taken at different time intervals (t=5, 10, 15, 30, 60 and 90 min), the time of the injection being t=0. A Perkin-Elmer Lambda 15 UV–Vis Spectrophotometer was used in the reflectance mode at λ=420 nm.

3. Results and discussion

3.1. Preparation of colloidal silver films

3.1.1. Fabrication of silver films by in situ formation of colloidal silver

The deposition rate of the silver film on glass was faster than that on PVC since a coherent film had been formed on glass by t=16 min whilst a coherent film had not been formed on the PVC substrate after 21 min had elapsed. Frens and Overbeek [3] postulated that the cores of colloidal silver particles produced by the 'Carey Lea' method [2] were positively charged. This may account for the faster deposition rate on glass compared with PVC since the glass will have a higher negative surface charge than PVC and will therefore have a higher electrostatic attraction for the colloidal silver particles.

From SEM studies the particles produced by this method were spherical and 80 to 180 nm in diameter (Fig. 1). This compares with 40 to 150 nm obtained by Ni et al. [7] using the same method on frosted glass slides.

Due to the ease of processing PVC this material was used in further studies, different thicknesses of silver films being produced by 'dip-coating' for different lengths of time.

3.2. Reaction of silver films with hydrogen sulphide

3.2.1. Preliminary screening

Vacuum deposited silver films (25 nm thick) and silver films prepared by dip-coating for 28 or 75 min were exposed to pure, dry hydrogen sulphide and observed visually. The vacuum deposited silver film initially (over the first 30 min) showed no observable change and after 1 h of exposure showed a slight surface discolouration. However the colloidally produced films reacted with the hydrogen sulphide more quickly, as evidenced by a change in colour from yellow/grey or silver to blue/black. The film fabricated by dip-coating for 28 minutes turned blue/black in ca. 10 min whilst the film fabricated by dip-coating for 75 min took 15 min to turn blue/black.

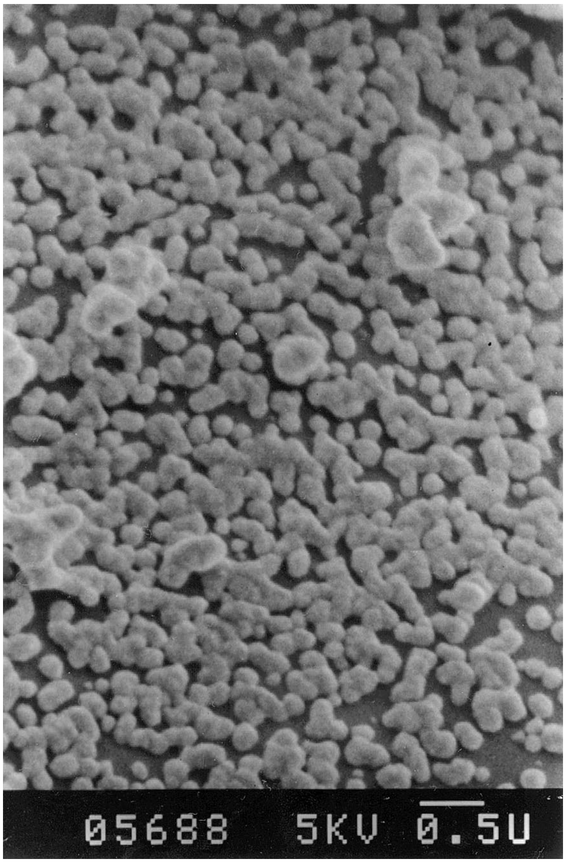

Fig. 1. Photomicrograph taken by scanning electronic microscopy of a colloidal silver thin film produced using Tollen's reagent with PVC as the substrate and a fabrication time of 35 min.

3.2.2. Reaction of colloidal silver film (fabrication time=28 min) with different concentrations of dry hydrogen sulphide

The colloidal silver thin films were exposed to three different concentrations of dry hydrogen sulphide (1 ppm, 10 ppm and 250 ppm in nitrogen) in a constant flow cell. After 150 min no change in absorbance was registered and no visual colour change could be appreciated.

3.2.3. Reaction of colloidal silver films (fabrication times 28 or 75 min) with different concentrations of hydrogen sulphide in the presence of water vapour

The colloidal silver thin films were exposed to different concentrations of hydrogen sulphide ranging from 0.1 ppm to 500 ppm at a relative humidity (RH) of 46–49% or 61–63%. The average initial absorbance at 420 nm of the films employed in these experiments was 0.311±0.003 arbitrary units for the films dip-coated for 28 minutes and 0.224±0.009 arbitrary units for the films dip-coated for 75 min. The films dip-coated for 28 min appeared yellow-grey in transmission whilst the films dip-coated for 75 min formed a silver mirror and were thus highly reflecting. The absorbances of various silver films (which had not been exposed to H_2S) were measured in order to estimate the error associated with taking the absorbance measurements: for films dip-coated for 28 min and 75 min the error was 0.003 units. Other potential sources of error in monitoring the rate of reaction between the silver film and H_2S are the variation in temperature and relative humidity and these two errors could not be easily estimated.

3.2.4. Relative humidity of 46–49%

Table 1 shows the measured absorbance values for the two different film thicknesses when exposed to H_2S at a relative humidity of 46–49%. For films that had been dip coated for 28 min the maximum absorbance change obtained was 56% (90 min exposure to 500 ppm H_2S). 90 min exposure to a hydrogen sulphide concentration of 200 ppm or 500 ppm gave comparable results (53% and 56% change in absorbance respectively). Films that had been dip-coated for 75 min gave larger absorbance changes at 90 min and the response of the films with increasing concentration of hydrogen sulphide did not reach a maximum (at 200 ppm the % absorbance change was 67% and at 500 ppm 84%). This observation could be explained by the fact that the mass of silver in the thicker film is greater and therefore the concentration of hydrogen sulphide at which the silver is totally reacted is higher, i.e. the saturation point, is not reached. In the case of films prepared by dip-coating for 28 min all the available silver is assumed to have been reacted when a concentration of ca. 200 ppm H_2S had been reached (for a reaction time of 90 min). Any higher concentration of the gas therefore gave the same percentage change in absorbance.

Humidity is known to play an important role in the reaction between hydrogen sulphide and silver. Water is essential for the reaction to take place and high humidity would enhance the rate of reaction

Table 1
Absorbance values (arbitrary units) obtained for two colloidal silver thin films when exposed to different concentrations of hydrogen sulphide at a relative humidity of 46–49% (– data not available)

Exposure time (mins.)	Concentation of H_2S					
	0.1 ppm	1 ppm	5 ppm	10 ppm	200 ppm	500 ppm
Sensor fabricated by dip-coating for 28 min						
0.0	0.303	0.298	0.310	0.328	0.313	0.316
5.0	0.302	0.305	0.338	0.370	0.353	0.353
10.0	–	–	0.343	0.376	0.373	0.372
15.0	0.318	0.317	0.348	0.386	0.397	0.396
30.0	0.313	0.328	0.359	0.428	0.425	0.439
60.0	0.319	0.347	0.377	0.453	0.458	0.461
90.0	0.328	0.359	0.389	0.467	0.478	0.494
Sensor fabricated by dip-coating for 75 min						
0.0	0.250	0.222	0.252	0.255	0.228	0.219
5.0	0.254	0.246	0.285	0.292	0.291	0.291
10.0	0.263	–	0.297	0.301	0.306	0.310
15.0	–	0.262	0.306	0.311	0.318	0.333
30.0	0.281	0.269	0.312	0.337	0.339	0.357
60.0	0.296	0.276	0.325	0.364	0.362	0.385
90.0	0.314	0.283	0.336	0.377	0.381	0.404

[15,18,19]. As shown earlier in this study no visual changes could be detected in colloidal silver films exposed to low concentrations (1–250 ppm) of dry hydrogen sulphide after 150 min. However the absorbance changed significantly at RH 46–49% even at concentrations of hydrogen sulphide as low as 0.1 ppm; for example a 26% absorbance change on exposure to 0.1 ppm H_2S for 90 min for films fabricated by dip-coating for 75 min.

3.2.5. *Relative humidity of 61–63%*

The same experiments were carried out in laboratory air when the relative humidity was 61–63%. Table 2 shows the measured absorbance values when films prepared by dip-coating for 28 or 75 min were exposed to low concentrations of hydrogen sulphide. At the higher humidity of 61–63% the change in absorbance was also higher. Comparing the results obtained for 1 ppm of H_2S at 90 min at the two relative humidities studied, an increase of ca. 14% in relative humidity gave an increase in % change in absorbance of ca. 3.2 times for films dip-coated for 28 min (from 20% at 46–49% RH to 66% at 61–63% RH). Similarly films dip-coated for 75 min showed an increase in % absorbance change of ca. 3.4 times on increasing the relative humidity by 14% (from 27% at 46–49% RH to 94% at 61–63% RH).

Table 2
Absorbance values (arbitrary units) obtained for two colloidal silver thin films when exposed to low concentrations of hydrogen sulphide at a relative humidity of 61–63% (–data not available)

Exposure time (mins)	Concentration of H_2S		
	0.1 ppm	1 ppm	10 ppm
Sensor fabricated by dip-coating for 28 min			
0.0	0.313	0.308	0.306
5.0	0.349	–	0.335
10.0	0.355	0.359	0.364
15.0	–	0.391	0.384
30.0	0.384	0.419	0.438
60.0	0.432	0.480	0.479
90.0	0.438	0.510	0.511
Sensor fabricated by dip-coating for 75 mins			
0.0	0.212	0.176	0.198
5.0	0.247	–	0.255
10.0	0.262	0.222	0.275
15.0	–	0.239	0.293
30.0	0.285	0.270	0.347
60.0	0.323	0.313	0.377
90.0	0.356	0.342	0.401

Again at a relative humidity of 61–63% saturation (i.e. total reaction of available silver) seemed to occur for the films that had been dip-coated for 28 minutes, since at 1 ppm H_2S the % absorbance change at 90 min was 66% and at 10 ppm H_2S, 67%. This saturation point occurred at a lower H_2S concentration than the saturation point at lower relative humidities of 46–49% when the plateau in % absorbance change at 90 min occurred at H_2S concentrations of $\geq$200 ppm. Films dip-coated for 75 min showed larger % absorbance changes than for films dip-coated for 28 min (103% change in absorbance for exposure to 10 ppm H_2S at 90 min c.f. 67%) as was observed at the lower relative humidity of 46–49%.

In general the first 5 min of exposure to H_2S gave the highest changes in absorbance (Fig. 2 and Tables 1 and 2). This fact corroborates the theory that the reaction is driven by the amount of silver available on the film, the rate of reaction being higher in the first stages of the reaction. A comparison of the experimental data for films dip-coated for 28 or 75 min at a relative humidity of 46–49% or 61–63% when exposed to 1 ppm of hydrogen sulphide (Fig. 2) showed that the optimum conditions for maximum sensitivity at this concentration of H_2S were: film fabrication time 75 min and RH 61–63%. For the latter conditions a visual change in colour of the silver film was observed after 10 min of exposure to 1 ppm of H_2S and after 60 min of exposure to 0.1 ppm of H_2S.

Fig. 3 shows the response obtained when the films were exposed to various concentrations of H_2S for 30 min at the two relative humidities. In general the greatest % change in absorbance occurs at low concentrations ($\leq$0.1 ppm H_2S) and the response starts to plateau out at a concentration of H_2S higher than 1 ppm.

Further tests were carried out monitoring colour changes of colloidal silver thin films exposed to other organic sulphide vapours. Dimethyldisulphide or ethanethiol was injected into a flask containing colloidal silver films, prepared by dip-coating for 28 min and 75 min, to give a final concentration of 100 ppm at a relative humidity of 50%. No colour changes could be visually detected after 90 min of exposure in either case.

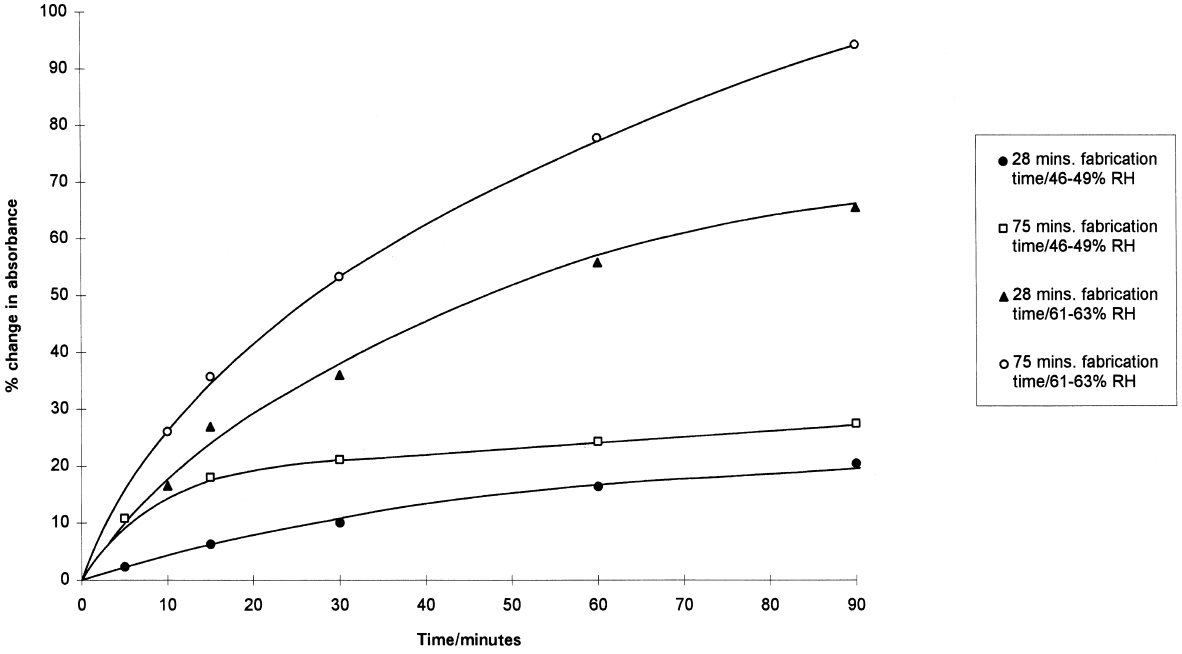

Fig. 2. % change in absorbance versus time for colloidal silver thin films prepared by dip-coating for 28 or 75 min when exposed to 1 ppm of hydrogen sulphide at a relative humidity of 46-49% or 61-63%.

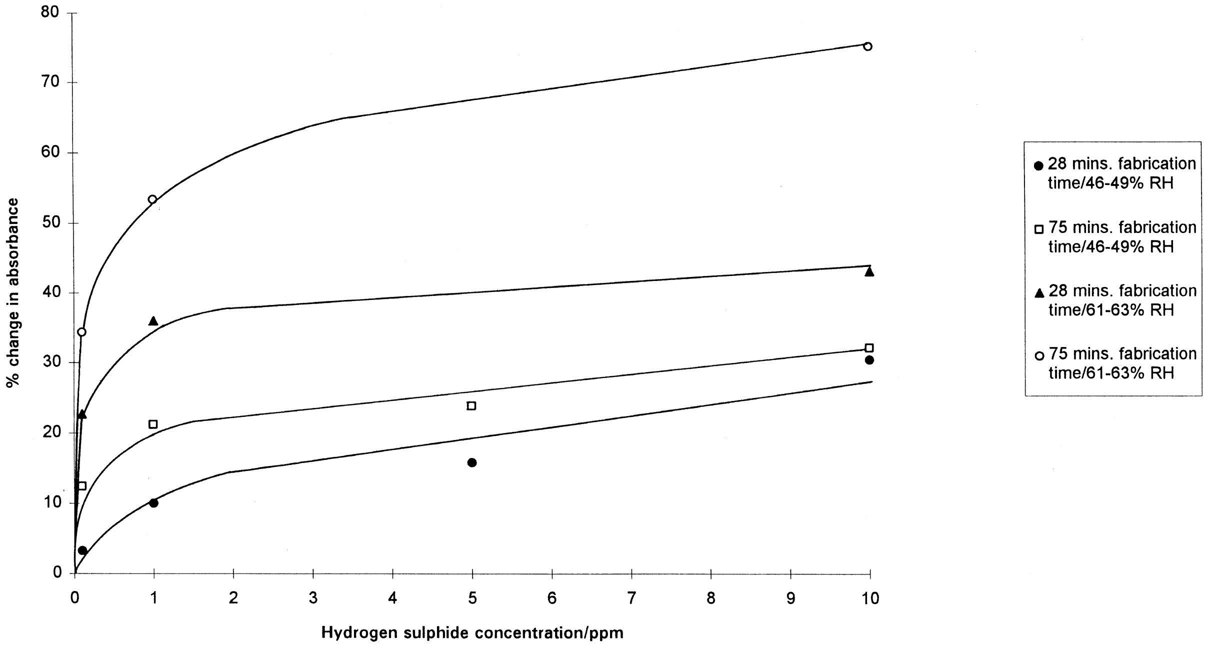

Fig. 3. % changes in absorbance after 30 min of exposure versus hydrogen sulphide concentration for colloidal silver thin films prepared by dip-coating for 28 or 75 min at a relative humidity of 46-49% or 61-63%.

4. Conclusions

Colloidal based silver films were successfully fabricated on PVC by a facile dip-coating method. We have shown that these films can be used as sensors for the detection of low concentrations of H_2S in controlled humidity environments. Absorbance changes at λ=420 nm could be detected when the thin films were exposed to H_2S concentrations as low as 0.1 ppm at a relative humidity of 61–63% after 5 min and colour changes could be visually detected for 1 ppm of H_2S after 10 min of exposure. The films were unresponsive to dimethyldisulphide and ethanethiol at concentrations of 100 ppm (relative humidity 50%).

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