



Glass for Nitrogen Oxide, Formaldehyde and Hydrogen Sulfide Molecules Detection

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Abstract

Simple and cost-effective glass sensors for detecting of the hazardous pollutant gases NO₂, formaldehyde and H₂S molecules are qualitatively explored. Porous glass pellets based upon soda lime glass were obtained by crushing, sieving and pressing the grains below 0.075 mm with a filler of soluble salt. The pellets were sintered at 700 °C for 15 min followed by removing of the filler, then dried. The dried pellets are either treated with appropriate reagents such as universal indicator, SnCl₂ or lead acetate for detecting NO₂, formaldehyde or H₂S molecules, respectively. In the case of treatment with universal reagent a red, brownish-red or orange coloration reveals the presence of NO₂, formaldehyde or H₂S molecules, respectively. Glass pellets treated with lead acetate turned into brown or blackish brown color indicating the presence of H₂S gas. Pellets treated with SnCl₂ show an increase in the electrical conductivity when subjected to formaldehyde gases or formaldehyde-containing solution. The increase in the electrical conductivity values is proportional to the exposure time of formaldehyde gas or the immersion time in formaldehyde-containing solution. The described method presents a simple, inexpensive and spread-able technique for detecting the NO₂, formaldehyde or H₂S molecules.

Keywords: Nitrogen dioxide, Formaldehyde, hydrogen disulfide, Glass sensors, Hazard compounds

Introduction

Recently, there is an increasing social sensitivity to environment and its pollution. Air is a potential source of risk where people live in urban and industrial regions. Many gases, without color and often without smell, are breathed every day at work, at home or on the road [1]. Hazardous gases can also be present in many forms such as food and drinks [2], agriculture [3], energy transportation [4] and industrial processes [5]. Attention is given to the problems related to the release of a large amount of toxin gases such as Nitrogen dioxide (NO₂), induced by imperfect combustion in automobiles and industrial zones [6,7] There is a need for reliable chemical sensors able to operate in harsh industrial environments such as metallurgy, glass, ceramic, paper, automotive, aerospace and energy. To fulfill these requests, emission monitoring sensors able to detect CO, CO₂, NO_x (NO and NO₂), hydrocarbons (HCs) and volatile organic compounds (VOCs) have been developed [7].

Formaldehyde is one of the most dominant pollutants in indoor environments, owing to a wide range of building materials and consumer products present indoors that emit formaldehyde and to a variety of chemical reactions that occur in indoor environments that generate formaldehyde [8,9]. Chronic exposure to formaldehyde is often of greatest concern in indoor environments, where concentrations may be four to ten times greater than outdoor concentrations [10]. Such exposure is associated with numerous hazardous health end points, including decreased pulmonary function, sensory and respiratory irritation, respiratory tract pathology, increased asthma incidence and increased damage to immune systems [11].

Hydrogen sulfide (H₂S), which is also referred to as sewer gas [12] is a highly poisonous and flammable gas. It commonly collects in enclosed places with inadequate ventilation, such as basements,

manholes, and sewer lines. It usually originates from bacterial decomposition of organic matter in anaerobic environments. It can also occur in geothermal systems, where it originates from magma degassing and thermal metamorphism [13]. Moreover, H₂S is produced as a by-product in more than 70 industries, including petroleum refining, Kraft paper mills, coal gasifiers, waste management, and natural gas production [14]. In low concentrations, it has the characteristic odor of rotten eggs. The odor is strongly offensive at concentrations as low as approximately 5 ppm. At concentrations above 100 ppm, the gas quickly paralyzes the olfactory nerves, and the sense of odor disappears. This can give the false impression that exposure to the gas was transient. In low concentrations (50 ppm), it is an irritant of the eyes and the entire respiratory tract. Prolonged exposure to moderate concentrations (250 ppm) causes the alveolar membranes to exude fluids that interfere with the normal exchange of gases. The principal symptom is asphyxia, which becomes apparent hours after exposure, and may lead to suffocation. Inhalation of high concentrations (1000 ppm) of H₂S paralyzes the respiratory nerve center, which can lead to suffocation. Physical collapse may occur without warning [15, 16].

Gas sensors play an undeniable role in most fields of technology in the modern world; they are broadly used for public safety, pollution monitoring, quality control, breath analysis, smart homes and automobiles. Due to their low cost, high sensitivity, compact size, online detection, ease of use, portability, and low power consumption [13]. Many materials based on polymers, composites and ceramics have been tested as gas sensors due to their own features and specific operating conditions. [17] Porous glasses (PG) can be used as environmental and biological sensors in the process of removing different impurities from gases, surface and ground water [18]. They can be prepared by different methods including, phase separation process, sol-gel process and crystallized process. They are important in a large number of fields and applications [19,20]. Chemical sensors are used in domestic appliances and air quality monitoring, as well as, for the early detection of hazardous chemical agents, to provide safety and security in public places and transportation systems. Yet, despite the high demand, major advances in these sensors in terms of simple structure, lower cost, better selectivity, durability and reliability are always needed [17]. The present work demonstrates a facile method for preparing porous glass with large surface area and its utilization as gas sensing materials for nitrogen dioxide, formaldehyde and hydrogen sulfide molecules.

Experimental

Preparation of base glass

A soda-lime silica glass of composition 15Na₂O, 20CaO, 65SiO₂ was prepared. The raw materials (chemical grade sodium carbonate (Na₂CO₃), calcium carbonate (CaCO₃) and washed silica sand (SiO₂)) were mixed and milled in an agate mortar for 10 min to homogenize

the mixture, prior transferring it into a platinum crucible. Then, the mixture was melted for 2h at 1350°C and the melt was quenched in air. The quenched glass was manually crushed in an agate mortar, sieved and the glass powder below 0.075mm was collected and used for the preparation of porous-glass pellets.

Preparation of the porous-sensing glass pellets

The porous glass pellets were prepared by a technique which depends on mixing inorganic soluble filler such as sodium chloride with soda lime glass powder. The mixtures were pressed and sintered at 700 °C for 15 min then the sodium chloride is removed by water dissolution, consequently the pores are formed. This method produced porous glass pellets with pores of average diameter between 5 and 300µm depending on the amount of the filler. The amounts of the filler were 0.0,12.5, 25, 50 and 75 (wt %) (Table 1), the samples obtained are given the numbers 1,2,3,4 and 5 respectively. Figure 1 shows an example for such pellets. For preparation of the sensing pellets for each hazardous chemical compound, their pellets were treated with appropriate reagent as mentioned later on in items 3.5-3.7.

Table 1: The density results of the porous glass samples. Measurements were carried out after the added NaCl was dissolved in water and dried.

Sample	No.1	No.2	No.3	No.4	No.5
NaCl (wt %)	0	12.5	25	50	75
Density (g/cm ₃)	2.3673	1.842	1.3847	1.1997	0.9155



Figure 1: A glass pellet prepared from very fine glass grains (- 0.075mm).

Chemical durability tests

The grain test technique was used. Solutions of 0.1 M HCl and 0.1MNaOH were used as the corroding solutions at 90 °C temperature. Testing periods chosen were 2, 4, 8 and 16 hours. The surface area was calculated by the equation given by Adams et al [21]. 1g sample grains (45-60 mesh) were weighed then put in a pre-weighed sintered glass crucible of the Jena G4 type. The latter and its content were placed in plastic containers with covers, each containing 250 ml of the leaching solution such that it covers the grains and the crucible. After the intended period the content in the

sintered glass crucible was washed with distilled water, followed by ether and transferred to an oven at 110°C for 2hs for drying. After cooling in a desecrator, the sintered glass crucibles were weighed and the total loss in weight was calculated.

Density measurement

The densities of samples with regular shaped pellets were determined in duplicates using 50 ml stainless steel Density Cup- Pycnometer at room temperature (25 °C). The weight of the displaced liquid (distilled water) determine the volume of the sample (cm³) and the density can be calculated using the following equation: Density = wt of sample (gm) / volume of sample (cm³). Where the volume of the sample is the difference between the volume (weight) of water that fills the empty pycnometer and the volume (weight) of the added water in the pycnometer in presence of the sample.

Scanning electron microscope (SEM).

The internal morphology of the porous glasses is explored by SEM. Scanning electron microscope (SEM) of Jeol JSM 840-A was used to study the pore morphology in the internal structure. Magnifications used were in the range 50x- 250x at acceleration voltage of 10kV. Samples were fractured and covered with gold before examination.

Spectrophotometer measurements

The UV-Vis reflectance spectra of the samples were recorded for the samples using a V-530 Jasco spectrophotometer in the range 400–1100 nm using a SLM-468 specular reflectance accessory.

Electrical conductivity measurements

The a.c. method was applied to determine the electrical conductivity using LCR Hi Tester (HIOKI, 3532-50, Japan) over a frequency range from 0.042 kHz to 1 MHz and temperature range from 25 to 300 °C. The temperature was determined using a copper/Constantan thermocouple in close proximity to the sample. The dielectric constant (ϵ'), the loss tangent ($\tan \delta$), and the ac conductivity (σ_{ac}) were determined based on the following expressions [22-24]:

$$\epsilon' = C d / \epsilon_0 A, \epsilon'' = \epsilon' \tan \delta, \sigma_{ac} = \omega \epsilon_0 \epsilon'',$$

Where C = measured capacitance of the sample (F), d = thickness of the sample (m), ϵ_0 = permittivity of free space equals $8.85 \times 10^{-12} \text{ F m}^{-1}$, A = Sample surface area (m²), ω = the angular frequency, $\tan \delta$ = the loss tangent which is obtained directly from the instrument.

Results and Discussion

Chemical durability

The used soda-lime silicate glass is a common type of glass. The foremost component is Silicon dioxide (SiO₂), supplemented with glass modifiers like Calcium oxide (CaO), and sodium oxide (Na₂O).

Other common compounds in the glass include aluminum oxide (Al₂O₃) and magnesium oxide (MgO). The results show (Figure 2) that after 16 h at 90 °C, a glass weight loss of 1.061 g cm⁻² in the alkaline solution, while in the acidic one it loses 0.106 g cm⁻². The present results are in accordance with the published data [25].

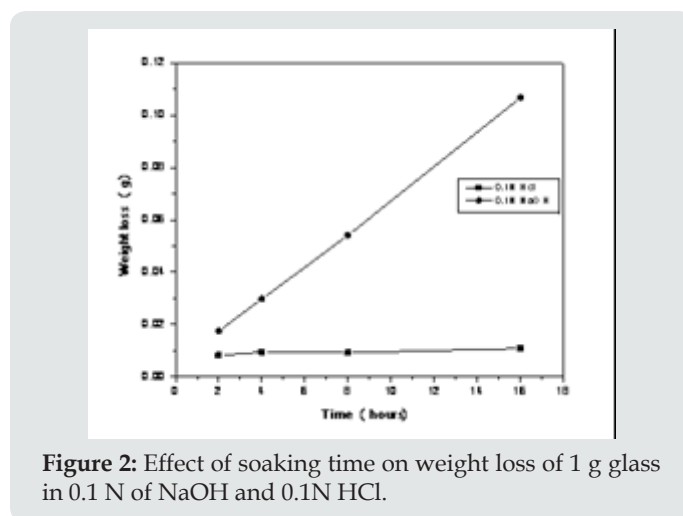
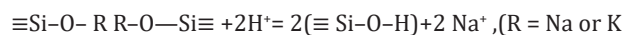
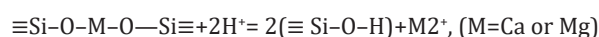
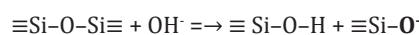


Figure 2: Effect of soaking time on weight loss of 1 g glass in 0.1 N of NaOH and 0.1N HCl.

When a glass probe contacts an acidic aqueous solution, the H⁺ ions of the medium replaces the modifier cations in the glass network, and the release of sodium, potassium and calcium is very low [26].



In alkaline medium breaking of Si-O-Si bond occurs as follows:



This increase in the leaching of the NWF groups always increases with time and with high rate (3).

Densities of the glass pellets

The Effect of preparation conditions on the densities of the glass pellets was studied. Samples with different content of filler prepared by the above described filling technique using (-0.075mm) grains were pressed at 5 KN and sintered at 700 °C for 15min. The sintered pellets were soaked in water to dissolve the filler. Figure 1 shows an example of such glass pellets. Table 1 shows the density values of the prepared pellets. The latter have densities in the range 1.8420 to 0.9155 (g/cm³), compared to 2.3673 g/cm³ for sample (No.1) without filling materials prepared under the same conditions. Table 1 reveals that sample No.5 with 75% filler has the lowest density which indicates presence of more pores after the removal of the filler in this sample.

SEM characteristics of the glass pellets

Figure 3 shows the SEM results of samples 1, 4 and 5 with filling and without filling material. The samples were prepared from (-0.075 mm) grains, pressed at 5 KN and sintered at 700 °C for

15 min. From the it can be seen that sample No.1 without fillings contains relatively few fine pores of 10-15 μm which may formed after the softening and reconnections of the glass grain boundaries. Sample No.4 with 50% fillings shows regular large pores of about

250-300 μm , while that of No 5 shows more pores of about 5 μm diameter. The decreased diameters of the pores for samples with 75% filler can be assigned to the crushing of the filler at such load (5KN) which gives rise to finer filler particles.

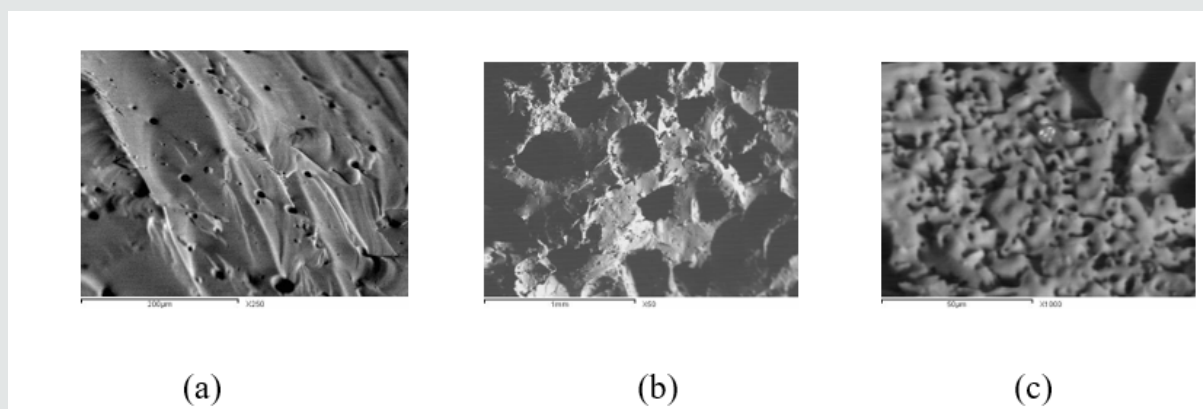


Figure 3: SEM of samples No.1 (a) without fillings, No.4 (b) with 50% fillings and No.5 (c) with 75% fillings.

Optical characteristics of the glass pellets

Figure 4 shows the optical reflection spectra of glass pellet samples with and without fillers. They are prepared from very fine glass powders (-0.075mm), pressed at 5KN and sintered at 700 $^{\circ}\text{C}$.

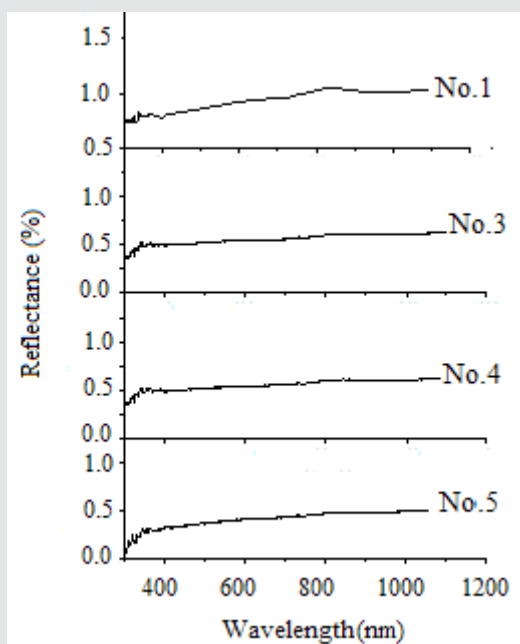


Figure 4: The Optical reflection spectra of sample (No.1) without filler and samples Nos. 3, 4 and 5 with 25 , 50 and 75 (%) filler, respectively.

Glass pellets for NO_2 detection

A porous glass pellet, which was previously treated with universal indicator, was dried at room temperature. The obtained dried pellet appeared green in color (Figure 5a) and acquired red coloration upon exposure to NO_2 gas for 2 Sec (Figure 5b). Nitrogen dioxide gas was evolved by reacting concentrated HNO_3 with a piece of copper metal placed in a tow-neck round flask. Universal

indicator is a mixture of various indicators, viz., Methyl red, methyl blue, Bromothymol blue, thymol blue and phenolphthalein. Besides these indicators, it contains water and n-propyl alcohol as solvents. They are both polar; they dissolve all the ingredients in the universal indicators [27]. NaOH is present in the mixture, which is acidic in nature, to adjust the pH of the indicator solution to give green colour at pH 7 [28].

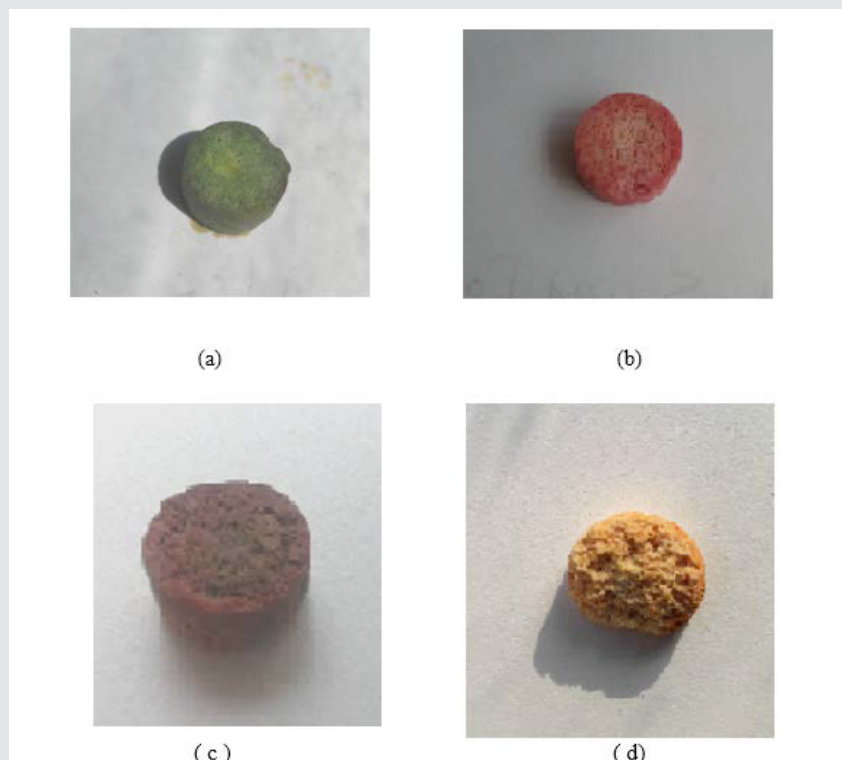


Figure 5: Glass pellet before exposure (a) and after exposure to NO_2 gas, red (b), to formaldehyde gas, brownish-red (c) and to H_2S gas, orange (d).

A porous glass pellet No.5 which was soaked in 5% solution of SnCl_2 and dried at room temperature, was introduced into a tow-neck round flask in which NO_2 gas is evolved. The glass pellet remained in the NO_2 gas for 1, 2, 3, 5, 10 and 20 minutes followed by electric conduction measurements. Figure 6 shows that the

change in their electrical conductivity is proportional to the time of exposure to such gas, which indicates the increase of amount of the adsorbed NO_2 . An abrupt increase in the electrical conductivity from 2.07×10^{-8} to 1.70×10^{-5} is noticed after 3 minutes exposure and reached 1.80×10^{-4} with lower rate after 20 min.

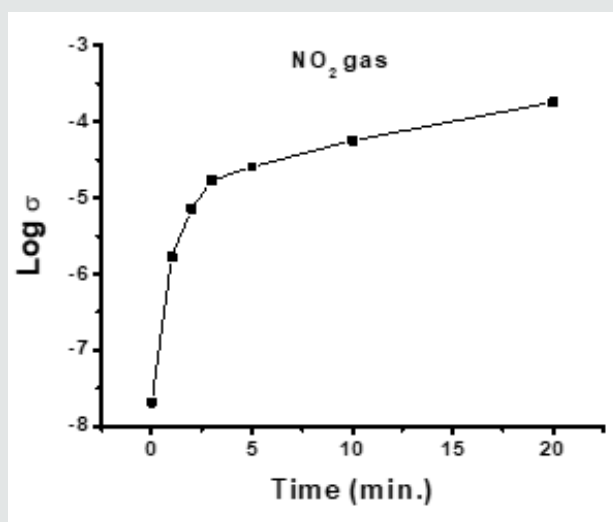


Figure 6: Variation of the electrical conductivity of the glass pellet exposed to NO_2 gas for different times. Measurements were carried out at room temperature.

Glass pellet for HCHO detection

The presence of gas formaldehyde was explored using a glass pellet that soaked in universal indicator and dried at room temperature (5a). When the pellet is subjected to the evolved formaldehyde gas the green color of the unexposed sample is change in this case into a brownish-red color (Figure 5c).

In other method, the electrical conductivity of porous glass No.5 soaked in 5% solution of SnCl_2 followed by drying at room temperature was tested after its exposure to formaldehyde gas. About 100ml of liquid formaldehyde (37% lab grade) was placed in tow-neck round flask placed on a hot plate (Figure 7), the temperature of which was raised gradually until formaldehyde gas was evolved in steady state (without causing boiling of the solution). The SnCl_2 treated pellet was exposed to the evolved formaldehyde gas for different times (1, 2, 3, 5, 10 and 20 minutes) and its electrical conductivity was measured after each exposure time. Figure 8 shows that increasing the time of exposure indicates presence of more adsorbed formaldehyde as the conductivity of the sample was increased from $2.07 \times 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$ which reached a value of $1.86 \times 10^{-4} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at about after 20 min.



Figure 7: A glass pellet hanged in HCHO gas.

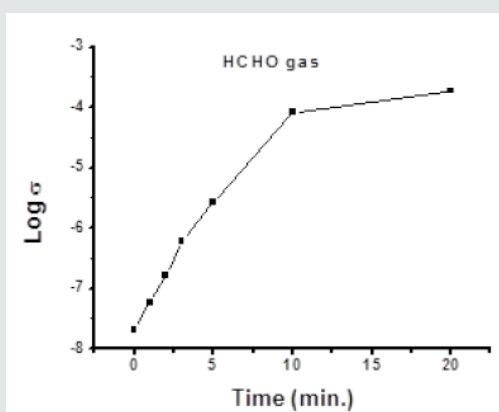


Figure 8: Variation of the electrical conductivity of the glass pellet exposed to HCHO gas for different times. Measurements were carried out at room temperature.

For detecting formaldehyde in aqueous solution, a glass pellet previously soaked in 5% solution of SnCl_2 followed by drying at room temperature was prepared. The obtained sample was immersed in distilled water for 15 seconds then the upper surface was dried by slight contacting with a filter paper. The electrical conductivity of the wetted sample was measured at room temperature and its value is considered as the starting value for the blank sample before being in contact with the formaldehyde-containing solution. Figure 9 shows the variation of electrical conductivity of the glass pellet after immersion in 5% HCHO solution for different immersion periods of time. Measurements were carried out at room temperature. The conductivity of the sample was increased from $7.67 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$ to reach a value of $1.89 \times 10^{-4} \text{ Ohm}^{-1} \text{ cm}^{-1}$ after 5 min. This increase in conductivity reveals presence of more adsorbed formaldehyde. The higher conductivity of the blank sample that used to detect formaldehyde in solution than that used for detection of gas formaldehyde can be attributed to the presence of water in the former sample.

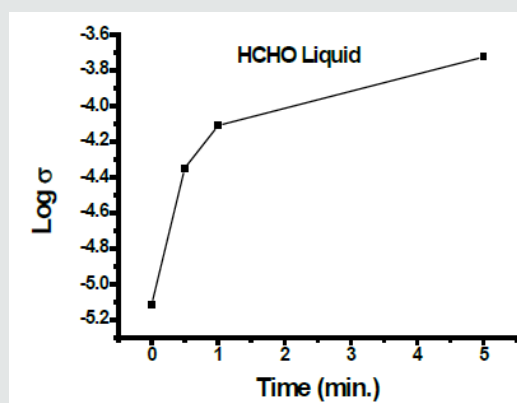
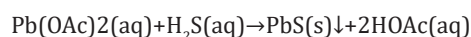


Figure 9: Variation of electrical conductivity of the glass pellet immersed in aqueous solution of HCHO for different periods. Measurements were carried out at room temperature.

Glass pellet sensitive to H_2S

A glass pellet, previously treated with universal indicator as described above, is used to explore the detection of H_2S gas which is colorless in nature. The green color of the glass pellet (Figure 5a) is changed to orange coloration upon exposure to H_2S gas (Figure 5d). However, lead acetate is more sensitive than any other method for detecting H_2S . It detects even traces of H_2S to produces lead sulfide, a black precipitate [29]:



Therefore, porous glass pellets were soaked in lead acetate solution then dried to be susceptible to detect H_2S gas [30]. The pellets treated with lead acetate were exposed to H_2S gas for different periods of times. Figure 10 shows that increasing the time of exposure from 1 second to 5 minutes produces more dark coloration from brown, to dark brown, to blackish brown. Figure 11

shows the optical reflection spectra of glass pellet No.5 measured before and after exposure to H₂S. It can be noticed that there is no reflection band in the range 300-1100 nm for the unexposed sample. Figures 11a & 11b shows that after exposure of the pellet

for H₂S gas for 10 sec, the color is changed from white into brown in color meanwhile the reflection spectrum is characterized by a broad optical absorption in the range 400-850 nm which explains the observed brown coloration.



Figure 10: Effect of H₂S gas on a porous glass pellet exposed to different periods.

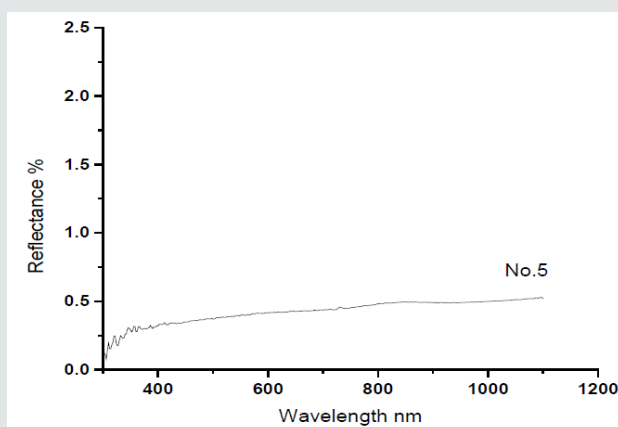


Figure 11: The reflection spectrum of glass pellet No.5 before (a) and after exposure to H₂S for 10 sec (b).

Conclusion

Porous glass based upon soda lime glass could be obtained by crushing and sieving. The grains below 0.075 mm were pressed with a filler of soluble salt into pellets which were sintered at 700 °C for 15 min followed by removing of the filler, then dried. The prepared pellets are characterized by pores of 1.5-330 μm and

densities in the range 1.8420 to 0.9155 (g/cm³). The dried pellets treated with universal indicator, SnCl₂ or lead acetate were able to detect NO₂, formaldehyde or H₂S molecules, respectively. Red, Brownish-red and orange coloration in case of universal reagent reveals the presence of NO₂, formaldehyde and H₂S molecules, respectively. Glass pellets treated with lead acetate turn into brown or blackish brown color indicating the presence of H₂S gas.

Pellets treated with SnCl_2 show an increase in the electrical conductivity when subjected to formaldehyde gases or formaldehyde-containing solution. The increase in the electrical conductivity values is proportional to the exposure time this gas or immersion in formaldehyde-containing solution. The described method presents a simple, inexpensive and widespread-able technique for detecting the NO_2 , formaldehyde or H_2S molecules.

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