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Electrochemical Sensing of H_2S Gas Based on Exfoliated Graphite/Chitosan Films laden Cadmium Ions

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ABSTRACT

The destructiveness of sulfide in its free hydrogen-sulfide form is distinguished to bring suffering to persons at its poorer concentration, while at its elevated concentration it may give a deficiency of consciousness, long-lasting brain damaging or even death through suffocation. In this study after preparing and characterizing Exfoliated graphite (EGt), functionalized graphite and Exfoliated graphite/chitosan, films have been prepared, and the cadmium ions were laden on it to be used in the detection of hydrogen sulfide gas electrochemically. The findings showed that a notable change in the electrical conductivity with a time of the films under investigation in response to gas adsorption. To determine the effect of the amount of EGt on the conductivity measurements at detection of H_2S gas in darkness and light we used various weights to know which is better. Furthermore, to determine the effect of H_2S gas concentration on the electrochemical conductivity of graphite (Gt) and EGt films, we passed different concentrations of gas every 15 minutes and measuring the electrical current. Furthermore, the graphite and Exfoliated graphite were examined by X-ray diffraction (XRD), and scanning electron microscopy (SEM).

1. Introduction

Hydrogen sulfide gas is hazardous, colorless, extremely toxic, explosive, corrosive, and flammable with a characteristic odor of rotten eggs [1, 2]. H_2S is frequently produced in various industrial activities [3]. It is produced naturally in crude petroleum, natural gas, hot springs, foods, and by the bacterial breakdown of human and animal wastes. It is also known as sewer gas, swamp gas, and manure gas. It is responsible for many accidents of exposure to toxic substances especially in the petroleum and natural gas industry, sewage treatment, landfills, coke ovens, tanneries and Kraft paper mills.

The health effects of H_2S depend on its concentration and exposure duration. Exposure to low H_2S concentration can lead to many critical health problems such as eye and throat injury, poor memory, dizziness and loss of sense of reasoning and balance. The safe maximum level for hydrogen sulfide gas exposure is 130 ppb [4]. Exposure to higher concentrations can lead to serious health issues including loss of smell, and blindness [5, 6]. When the concentration of H_2S is greater than the olfactory perception threshold of 300 ppb, it will harm human health and induce nausea, headache, and lung irritation [7].

Even chronic, low-level exposures can also lead to irreversible health effects [8, 9].

At very high concentrations nearly 1000 ppm and above, H_2S immediately leads to death [10-12]. Hence, H_2S gas detectors and their performance, accuracy and quality are essential to save lives. Therefore, it has become a necessity to develop highly sensitive sensors, this is achieved through developing H_2S gas sensors that have compelling advantages such as low power consumption, low cost, and operating at room temperature to detect low levels of H_2S [13].

A variety of materials and methods have been used for H_2S gas detection [14]. One of the most popular sensing methods of detecting H_2S gas is the electrochemical sensor, and optical methods are used in sensing technologies. Electrochemical sensors are based on electrolytes, which are divided into solid and liquid electrolytes. Electrochemical sensors operate by the interaction of the gas of interest to produce an electrical signal that's proportional to the concentration of the gas. The produced signal serves as a further divider of these sensors into amperometric and potentiometric sensors. Amperometric sensors produce the current signal (rate of the electron transfer) as a function of time, which is proportional to the concentration of the analyte by Faraday's law and the laws of mass transport. These amperometric sensors are used to detect different gases [e.g., CO, NO_2, O_2, glucose and many others besides the hydrogen sulfide gas]. On the other hand, potentiometric sensors use ion selective electrodes to obtain the potential signal, which is logarithmically proportional to the concentration [15, 16].

The impetus for measuring and detecting hydrogen sulfide gas is protecting the personnel from the lethal effects of H_2S. Metal oxide semiconductors and metal salts have lately been used as materials in several gas detectors [17-23]. These detectors are based mainly on a conductivity response to hydrogen sulfide gas [24-28].

The illumination can affect the rate of adsorption and its time dependency, either increasing or decreasing the rate. Furthermore, the activation energy may be altered by illumination. Most studies of heterogeneous photocatalysis were done utilizing visible or near-ultraviolet radiation [29].

In this study, chitosan will be extracted from shrimp shells, and the cadmium metal will be loaded on a film of obtained chitosan, then it follows by hydrogen sulfide gas detecting utilized cadmium loaded chitosan membrane in the absence and presence of illumination.

2. Materials and Methods

2.1 Materials and pretreatment

A one liter of standard solution of chitosan was prepared by dissolving 1.0 gm in 75 ml of 2.0 % acetic acid. The solution was kept in a glass bottle for further use.

A 1.0 M solution of Cd (II) was prepared by dissolving $CdCl_2$ (1 mol, 183.32 g) in 1000 mL standard volumetric flask with deionized water.

2.2 Preparation Exfoliated graphite (EGt)

Graphite rods were collected from spent carbon-zinc dry cells, and the rods were thoroughly washed with nitric acid, followed by distilled water, and dried in an oven for 3.0 hrs at 120°C. Exfoliated graphite (EGt) was prepared by the electrochemical method. Briefly, two graphite rods taken from dry spent carbon-zinc cells were used, one as the cathode and the other as the anode. The electrodes were placed perpendicular to the electrochemical cell with a distance of 2.0 cm between them in 50 mL of sulfuric acid (13.5% H_2SO_4) as the electrolyte Fig. 1. The electrochemical peeling process was started when a DC voltage of 6.0 V and a current of 1.0 A were applied across the electrodes for a period of 3.0 hrs during the anode wear time. Exfoliated graphite was filtered and washed with distilled water until the filtrate was pH 7.0 and then dried in an oven at 50 °C.

2.3 Preparation of electrochemical detector

A known amount of EGt, 2.0 mL of standard chitosan solution, 0.1 mL of $CdCl_2$ (1.0 M), 0.1 mL of HCl (0.2 M) solution, and 0.1 mL of glycerol were mixed all together in a beaker. The resulting mixture was then poured onto a 4.0 cm^2 glass slide which was rested at room temperature to dry. The film formed was dried in an oven at (50 °C).

2.4 Electrochemical methods for detecting of H_2S gas

To perform the gas measurements, the Gt and EGt sensors laden cadmium ions were positioned in a test chamber, equipped with a glass window, controlling the composition of the inside atmosphere with the flow-through technique. Illumination was provided by the light produced by

eurolux spiral lamp (26 Watt), focused on the film through the glass window utilizing an optical system. The electrical conductance of the films was constantly monitored during gas measurements employing proper electronics interfaced to a data-acquiring system Fig. 2.

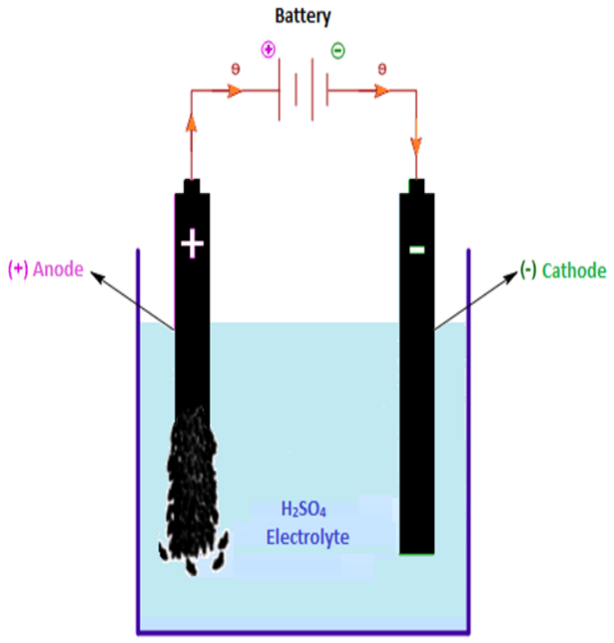

Fig. 1 Exfoliation of graphite process

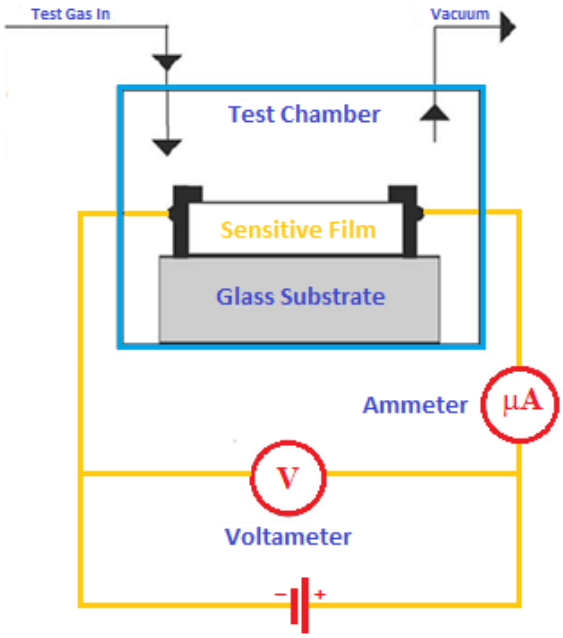

Fig. 2 Electrochemical method for detecting H_2S gas

3. Results and discussion

3.1.1 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) was employed to analyze the graphite obtained from the electrochemical exfoliation (EGt) at accelerating voltage 15 kV and magnification 12,000X. The morphologies of graphite powders before and after expansion were given in Fig. 3.

Fig. 3, shows the scanning electron microscopy SEM images of both original and expandable graphite (Gt), and electrochemically treated graphite or (EGt). We can notice a clear difference in graphite before and after the exfoliation process. SEM images reveal that the obtained product consists of a large amount of exfoliated or expanded graphite which is distinguished from the original sample by a significant difference in thickness of the graphite layers, it appears as loose and porous [30].

3.1.2 X-ray diffraction (XRD)

Exfoliated graphite obtained by treating it with concentrated sulfuric acid is evident in X-ray diffraction. Fig. 4 shows the XRD patterns of expandable graphite and the exfoliated graphite. It can be seen from XRD patterns that the diffraction peak of the exfoliated graphite is slightly shifted to a lower diffraction angle compared with the pattern of expandable graphite, indicating an increase in the interplanar spacing determined from Bragg's law ($2d\sin\theta = n\lambda$). The peak intensity of the EGt is decreased compared with that of expandable graphite due to the delamination of pristine.

3.2 Electrochemical sensing of H_2S gas

3.2.1 Electrochemical conductivity and gas sensitivity

Electrical resistivity is the resistance to the flow of an electric current with some materials resisting the current flow more than others. While a conductor resistance gives the amount of opposition it presents to the flow of electric current, the conductance of a conductor indicates the ease by which it allows electric current to flow. Conductivity is the efficiency of a conductor to pass electric current, thus the material that has a high conductivity will have a low resistivity, and vice versa. The resistivity and conductivity can be calculated from the following equations:

$\rho = R \times A/L$ (1)

$\sigma = 1/\rho$ (2)

where L is length (m), R is resistance (Ω), A is area (m^2), then ρ, σ are resistivity and conductivity respectively.

3.2.2. Sensitivity of Gt and EGt films loaded with cadmium ions to hydrogen sulfide gas in dark and light

Determination of the electrical conductivity of un-exfoliated graphite (Gt) films loaded cadmium ion mainly results in the investigation of its sensitivity on electrical responses when exposed to H_2S gas in illumination increases in electrical conductivity is observed from 0.033 to 0.055 $\Omega^{-1}m^{-1}$, followed by a decline, as shown in the Fig. 5. The same behavior is observed when using EGt, where the electrical conductivity starts from 0.045 to 0.078 $\Omega^{-1}m^{-1}$. By comparing the electrical conductivity values, it was found that EGt has better conductivity than Gt.

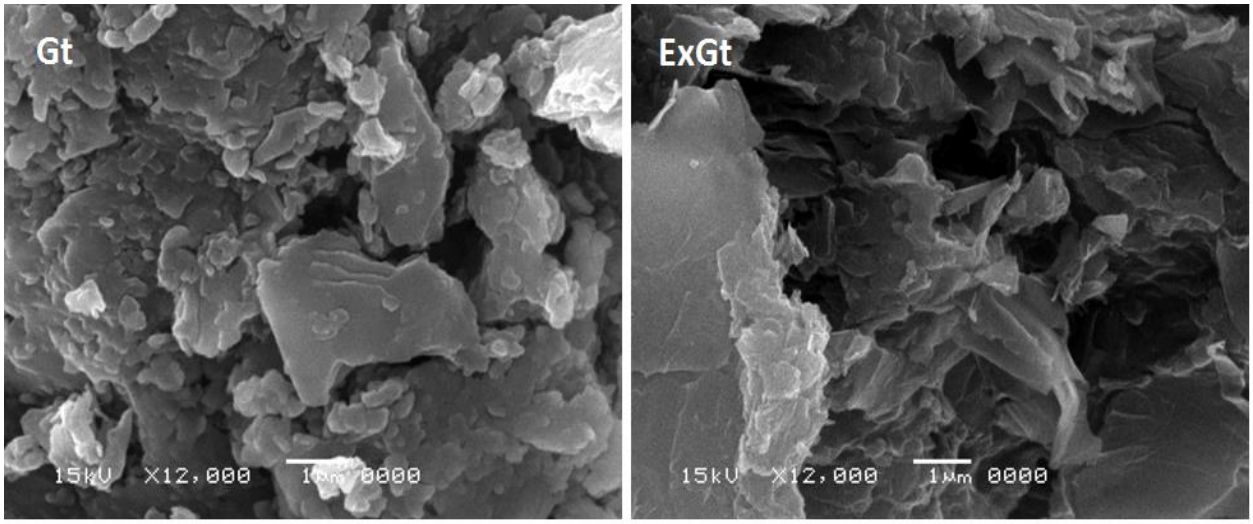

Fig. 3 SEM images of both original graphite (Gt), and electrochemically treated graphite (EGt)

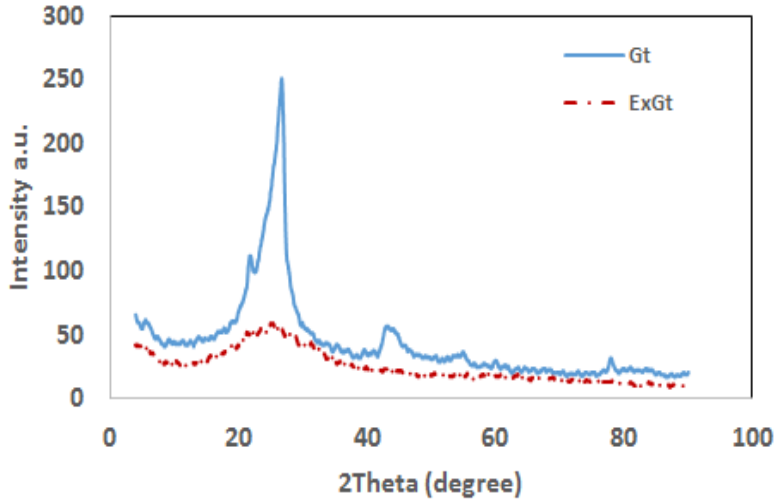

Fig. 4 XRD patterns of expandable graphite and the exfoliated graphite

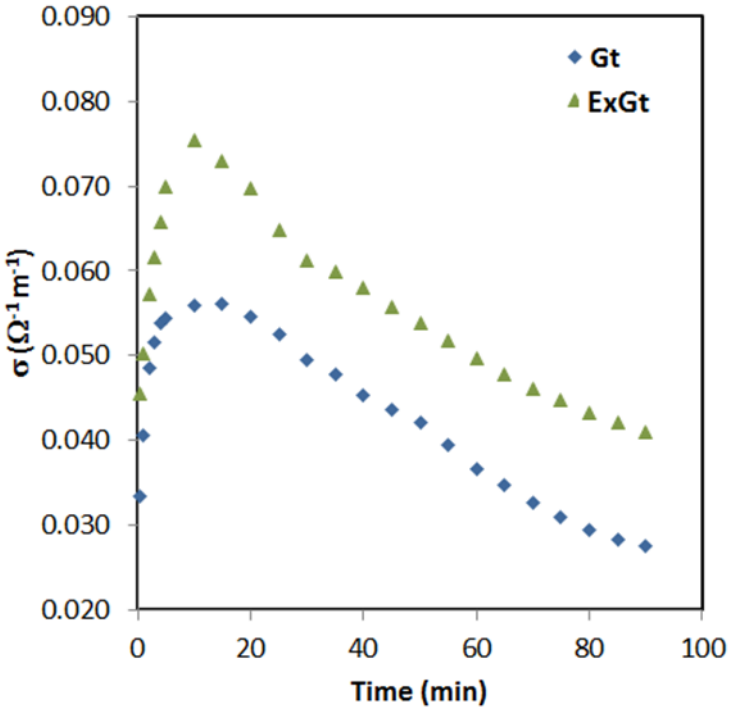

Fig. 5 Detection of hydrogen sulfide gas using Gt and EGt films loaded cadmium ions

3.2.3 Effect of amount of EGt on the conductivity at detection of hydrogen sulfide gas in darkness and light

EGt was chosen to study the effect of its quantity on the *detection* of H_2S gas, considering that it is better in sensitivity than Gt. To determine the effect of the amount of EGt on the conductivity measurements at detection of H_2S gas in darkness and light has been used five different weights of EGt which are 0.05, 0.10, 0.15, 0.20, and 0.25 g.

The electrical conductivity in the darkness increases with the amount of EGt, where the smallest amount of EGt (0.05 g) is the lower in electrical conductivity about 0.014 $\Omega^{-1}m^{-1}$, and it increases respectively till the higher amount (0.25 g), which it has higher conductivity about 0.06 $\Omega^{-1}m^{-1}$. EGt exhibits the same behavior in the presence of light, but the electrical conductivity was greater values, as the height of its peaks was at 0.02, 0.039, 0.053, 0.062, and 0.076 $\Omega^{-1}m^{-1}$ for the quantities used of EGt 0.05, 0.1, 0.15, 0.2 and 0.25 g, respectively.

The maximum response of a detection to H_2S gas after 15 minutes of exposure, is reported in Figs. 6 & 7. As a consequence of the electro-optical properties of CdS, illumination of the films increased the electrical conductivity which depended on the energy of the impinging radiation [31, 32].

3.2.4 Influence of gas concentration and limit of detection

To determine the effect of H_2S gas concentration on the electrochemical conductivity of Gt and EGt films, their done by passing different concentrations of gas every 15 minutes and measuring the electrical current each time at a constant voltage set at 5.5 V, the experiment was carried out under the influence of light. Fig. 8, shows the relationship between the change in gas concentration and the change in current intensity Fig. 8a, and the change in conductivity Fig. 8b.

The electrical current and electrochemical conductivity increase with the amount of H_2S gas until a steady-state (limit of gas concentration detection) which equals approximately 4.0 mmol of H_2S gas, that means the saturation of the films with gas and the completion of the reaction of all cadmium ions loaded on Gt and EGt films.

4. Conclusion

In this study after prepared and characterized Exfoliated graphite (EGt), functionalized graphite and Exfoliated graphite/chitosan films have been prepared, and the cadmium ions were loaded on it to be used in

the sensing of hydrogen sulfide gas electrochemically. The results showed that a remarkable variation in the electrical conductivity with a time of the films under investigation in response to gas adsorption; where (EGt) has better conductivity than (Gt). We used five different weights which are 0.05, 0.10, 0.15, 0.20, and 0.25 g. To know the effect of the amount of (EGt) on the conductivity measurements at detection of H_2S gas in darkness and light. The conductivity in darkness and light increases with the amount of (EGt), till the higher amount (0.25 g); which it has higher conductivity about 0.06 $\Omega^{-1}m^{-1}$. And the electrical conductivity having greater values in light than in darkness. The electrical current and electrochemical conductivity increases with the amount of H_2S gas until the saturation state which equals approximately 4.0 mmol of H_2S gas.

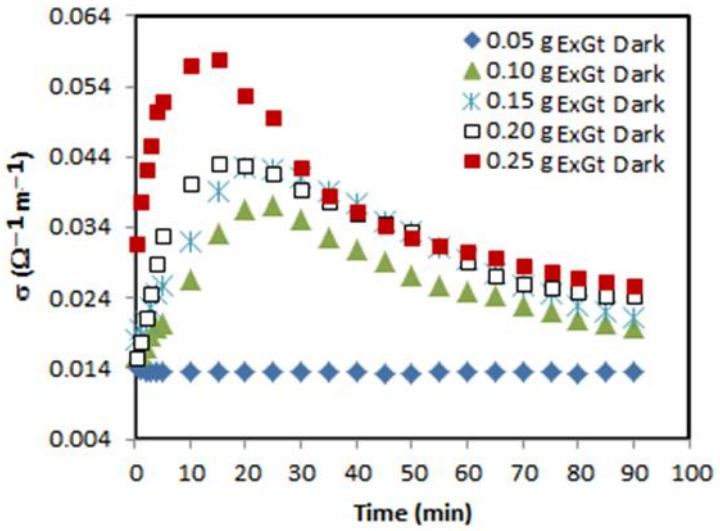

Fig. 6 Effect of amount of EGt on the conductivity at detection of hydrogen sulfide gas in darkness

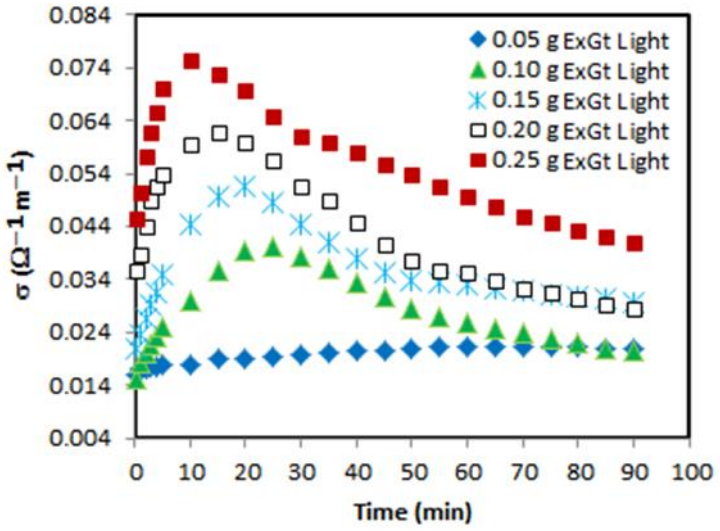

Fig. 7 Effect of amount of EGt on the conductivity at detection of hydrogen sulfide gas in light

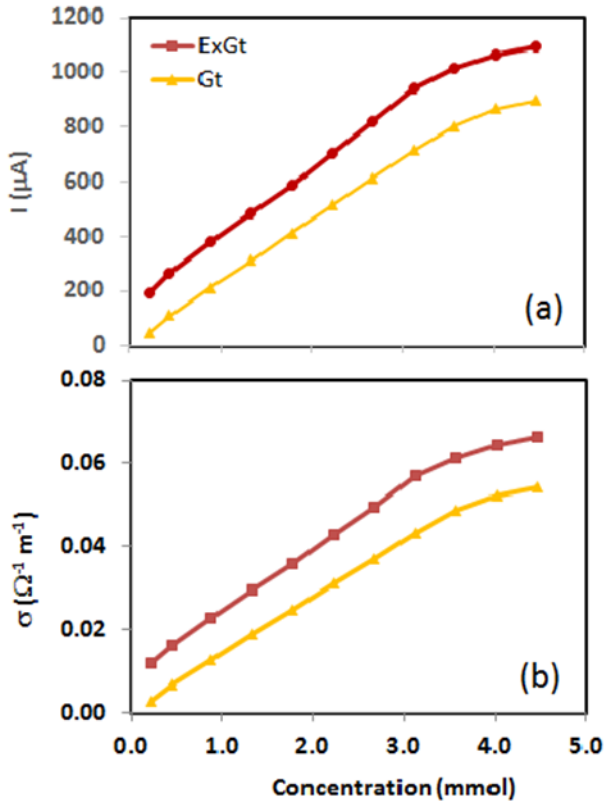

Fig. 8 The effect of H_2S gas concentration on the electrochemical conductivity of Gt and EGt films

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