Egypt. J. Chem. **Vol. 65**, No. 5 pp. 185 - 192 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Electrochemical Detection of H_2S Gas Based on Chitosan Extracted From Shrimp Shells Loaded Cadmium Ions

Mahmoud I. Aboushouk,* Adham A. El-Zomrawy,* Ahmed M. Salem

Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, 11884, Cairo, Egypt.

Abstract

The harmfulness sulfide in its free hydrogen of sulfide form is recognized to bring personal suffering at its lower concentration while at its higher concentration it may give a loss of awareness, permanent brain harmful or even death through asphyxiation. In this study after prepared and characterized chitosan, 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, in absence and presence illumination, with the time of the films under investigation in response to gas adsorption. Furthermore, the films were examined after the adsorption process of gas in many ways; resistor-capacitor circuit, thermo gravimetric analysis (TGA), FT-IR spectroscopic analyses, and scanning electron microscopy (SEM), were used to characterize the samples, and appear the differences before and after gas adsorption process.

Keywords; Chitosan, Electrochemical detection, Hydrogen Sulfide, sensor, cadmium.

1. Introduction

Hydrogen sulfide (H_2S) was only known as a harmful environmental pollutant a product ofdecaying matter, colorless, toxic, explosive, corrosive [1] and flammable gas with a characteristic smell of rotten eggs [2]. It is existed in groundwater, hot springs, volcanic gases, natural gas, and crude petroleum. It is characterized as very toxic to living organisms and plants. It can be exposed easily at a level of 0–5 ppm in the air. When hydrogen sulfide concentration reaches 10 ppm, it can affect human health [3-11]. Iodometric titration and methylene blue colorimetric assays have been the most common means of measuring H_2S [12, 13]. Traditional methods for H_2S measurement include fluorescence imaging, colorimetric sensing, and chromatographic techniques, such as high-pressure liquid chromatography (HPLC) and gas chromatography (GC) [14–21].Gas sensors are chemical sensors, which utmost importance. A chemical sensor encompasses of a transducer and an active layer to convert chemical information into the electronic signal like frequency, current, or voltage change. As the air surrounding us contains different species and amounts of gases and atmospheric pollutants that result from industrial or medical operations, which could be dangerous to human health, therefore it has become necessary to detect the presence of these gases because the environment consists of humans, plants, and animals, thus maintaining their safety and lives is top priority.Several gas sensor technologies are used for different gases detection including semiconductor, catalytic, electrochemical, optical and acoustic gas sensors. The performance characteristic of any sensor is based on some properties such as sensitivity, selectivity, detection limit, response time, and recovery time [22].Metal oxide semiconductors and metal salts have recently been utilized as materials in many gas sensing [23-28]. These sensors are based primarily on a conductivity response to H_2S [29-33]. Bio-polymers are appearing as a promising substitute for synthetic polymers for use in electrochemical devices due to many peculiar

*Corresponding author e-mail: aboushouk_m83@yahoo.com;azomrawy.1@azhar.edu.eg.
Receive Date: 25 September 2021, Revise Date: 26 October 2021, Accept Date: 07 November 2021
DOI: 10.21608/EJCHEM.2021.97670.4568

properties such as using chitosan in hosting ionic conductivity in batteries, super capacitors, dye sensitized photovoltaic and fuel cells [34, 35].

Chitosan is a natural, translucent, biopolymeric chemical compound consisting of a polysaccharide, derived from chitin found in a variety of natural sources, where it is the structural component of crustaceans, insects, and chitin is also found in the cells of fungi and some algae. Chitin is the second most abundant natural biopolymer in nature after cellulose [36]. Chitosan is a natural biocompatible, biodegradable and nontoxic polymer. It is one of the best types of thin composite film fabrication due to its superior films-forming properties, and ability to bind cationic and anionic forms of noble and transition metal ions [37-39]. Additionally, many chitosan based materials exhibit electrical conductivity; it is very versatile for chemical modifications for production of sensors and electrochemical devices, and also presents good interaction with different ions. All these properties allow the development of a wide range of applications [40-42].

The illumination can influence the adsorption rate and its time dependence, with a positive effect (increasing it) or with a negative effect (decreasing it).Moreover, also the activation energy may be changed by illumination. Most of the studies of heterogeneous photocatalysis were made using visible or near-ultraviolet radiation [43].

In this investigation, we will extract chitosan from shrimp shells and load the cadmium metal ion on the obtained film, and studying the detection of hydrogen sulfide gas using the cadmium loaded chitosan film in absence and presence illumination.

2. Experimental

2.1. Preparation and Characterization of Chitosan

The shrimp shells were washed with tap water many times, then dried under sunlight at ambient temperature (30±2 ºC) for three days until completely drying and cracked in blender then kept in a polyethylene bottle to start the chemical extraction of chitosan. Isolation of chitosan the following steps, namely demineralization, deproteinization and deacetylation (Fig. 1).

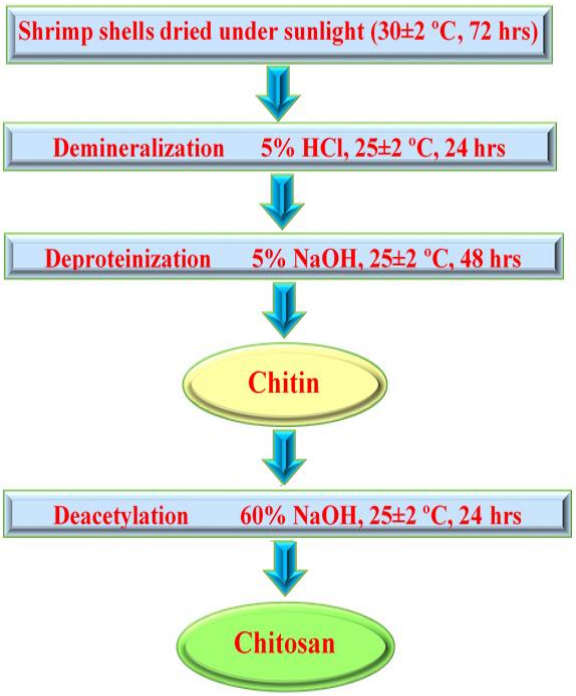

Fig. 1: extraction of chitosan

2.1.1. Demineralization

Shrimp shells were demineralized with a concentration (5.0 %) of HCl at room temperature (25 °C) with a solid to solvent ratio 1:6 (w/v) for 24 hours. The residue was filtered and washed with distilled water until pH 7.0, then dried in an oven at 60 ºC.

2.1.2. Deproteinization

Deproteinization of the yield was done with 5.0 % NaOH at ambient temperature (25 ºC) with a solid to solvent ratio 1:10 (w/v) for 48 hours. The residue was filtered and washed with distilled water until pH 7.0, then dried in an oven at 60 ºC and ground in blender. Then purified chitin was ready to deacetylation process.

2.1.3.Deacetylation

Finally; remove of acetyl groups (*Deacetylation)* from chitin to get chitosan was done with concentration of NaOH 60 % with a solid to solvent ratio 1:10 (w/v) at ambient temperature (25 ºC) for 24 hours. The residue was filtered and washed with distilled water until pH 7.0, then dried in an oven at 60 ºC.

2.2. Materials and pretreatment

A stock of chitosan solution was prepared by dissolving every 1.0 gm in 75 mL of 2.0 % acetic acid, we prepare one liter in a glass bottle with screw closer top and keep it for further use.Cadmium chloride solution was prepared by dissolving 183.32 gm of cadmium chloride salt in 1000 mL standard volumetric flask with deionized water. The primary stock solution thus had about 1.0 M of Cd (II) in solution.

2.3. Preparation of electrochemical detector

To prepare the electrochemical detector, 2.0 mL of 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. The mixture was poured onto a 4.0 cm^2 glass slide, and the film was dried in an oven at (50 °C).

2.4. Electrical methods for detecting H_2S gas

In order to evaluate the H_2S gas detecting characteristics of Ch film we followed the two-probe technique of resistivity measurement, where two electrical contacts were made on the Ch film by graphite electrodes conected with copper wire, and the cell was fed with a DC voltage of 5.5 volts. The electrically wired Ch film was enclosed in a gas chamber (100 ml) as per simulated diagram circuit in Fig. (2a), the H_2S gas was obtained by adding hydrochloric acid to ferric sulfide. Subsequently, the change in resistivity of the film was measured by passing H_2S gas through the glass chamber at a fixed flow rate. The experiment takes place in absence and presence of illumination, using eurolux spiral lamp, 26 watt.

2.5. Resistor–capacitor circuit (R-C circuit) tests:

The films are checked after being used in gas detection by Resistor–capacitor circuit. R-C circuit is an electric circuit composed of resistor and capacitor driven by a voltage or current source. The simplest R-C circuit consists of a charged resistor and capacitor connected together in a single loop. When we connect a voltage source to the R-C circuit, the voltage source charges the capacitor, and when the voltage source is disconnected and the circuit is closed, the capacitor discharges the charges coming from the voltage source into the resistance. When the circuit is connected, the stored capacitor energy through the resistor begins to discharge with time, depending on a constant which called the time constant (τ). In this electrical circuit, the resistor was replaced by the films under investigation (Fig. 2b).

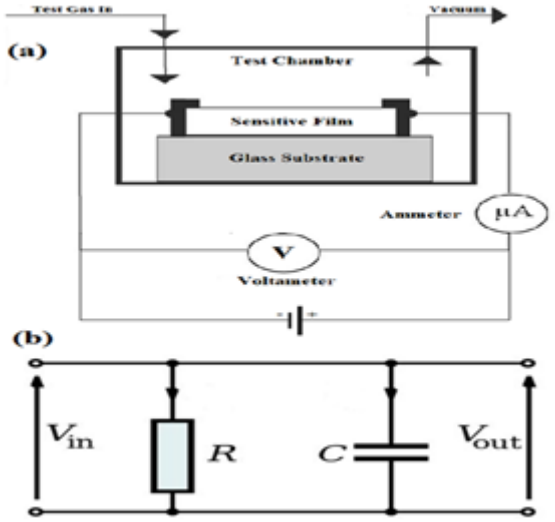

Fig. 2: (a) Electrochemical method for detecting H_2Sgas, (b) Resistor–capacitor circuit.

3. Results and discussion

3.1.1. Infrared Spectroscopic Analysis (FT-IR)

Characteristics of chitosan from chitin yield (71.4 %). The major absorption band is found between 1200 cm^{-1} and 1020 cm^{-1} which represent the free amino group (NH_2) in the C2 position of glucosamine, a main group present in chitosan. The sample showed further absorption bands at the various peaks 1020 cm^{-1} for C-O, 1430 cm^{-1} for $–CH_3$ in amide group,1570 cm^{-1} for –NH (amide II), 1650 cm^{-1} for C=O, 2927cm^{-1} for $–CH_2$, 3440 cm^{-1} for –OH and amide -NH, which are similar to the standard chitosan [44] as shown in Figure 3, and the broad band is due to intermolecular hydrogen bonding of the chitosan molecules, [45,46].

3.1.2. Thermo Gravimetric Analysis (TGA)

The thermal stability and composition of chitosan was obtained through TGA (Fig. 4). The results show, the degradation occurs in two stages. The first one from 60-100 ºC and is related to the losses of water. The polymer-water interaction is differ from each polymers and is related to the macromolecular structure and the crosslinked degree [47]. Determine that for low water contents, water molecules are bonding mainly to the amine groups which are easily removed (low temperature) when compared to the crosslinked polymers where water molecules are bonded to hydroxyl groups. The second stage from 250-350 ºC for chitosan crosslinked polymer and is related to the oxidation and thermal degradation, vaporization and elimination of volatile compounds [47]. The pyrolysis of chitosan starts as a random

split of glycosidic bonds and followed by a decomposition to small acids like butyric and acetic acids and a chain of lower fatty acids (C2, C3 and C6) [48].

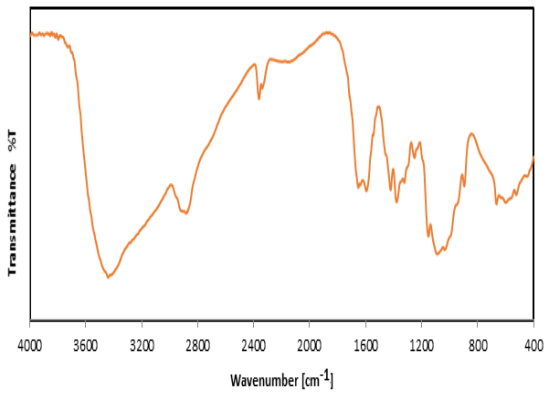

Fig. 3: FT-IR spectrum of chitosan

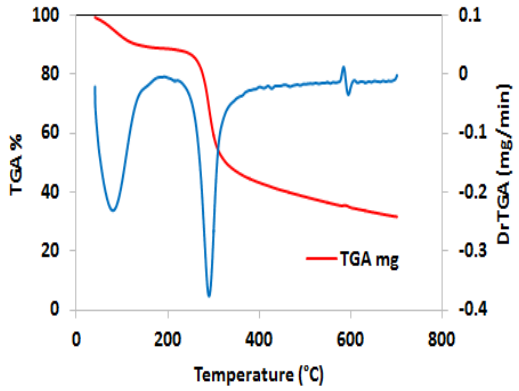

Fig. 4: TGA of chitosan

3.2. Electrical detecting of H_2S gas

3.2.1. Electrical resistivity, conductivity and gas sensitivity

The electrical resistance of a material is the resistance to the flow of electric current passing through it. While a conductor resistance gives the amount of resistance it offers to the flow of electric current, conductivity of a conductor indicates the ease with electric current is allowed to flow. The conductivity is the efficiency with which a conductor passes an electric current or signal without resistance loss, so a material or conductor that has a high conductivity will have a low resistance, and vice versa.. The resistivity and conductivity can be calculated from the following equations:

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

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

where R is the resistance in ohms (Ω), L is the length in meters (m), A is the area in square meters (m^2), the proportional constant ρ is the Resistivity, and σ, is the conductivity.

3.2.2. Detection of hydrogen sulfide gas using Chitosan films loaded cadmium ions in dark and light.

The study of the response of chitosan films to sensitive of the hydrogen sulfide gas (H_2S) was measured by electrical conductivity measurements against time at 25 °C (Fig. 5). For the chitosan blank (Ch), a slight change was observed in the behavior of chitosan (Ch), but it is discoverable, and this is shown by a slight increase in electrical conductivity with time.

The determination of electrical conductivity of cadmium- loaded chitosan films mainly results in the investigation of its sensitivity and selectivity on electrical responses when exposed to H_2S gas in dark and light. In the light a significant increase in electrical conductivity starts from above 0.0035 to 0.0040 $\Omega^{-1}m^{-1}$, as shown in Figure 5.

The increases in the electrical conductivity is due to the adsorption of gas onto the surface of the cadmium-loaded chitosan films, and then a chemical reaction that occurs between H_2S gas and cadmium ions on the surface of the films to form cadmium sulfide, which has a high conductivity. The increase in conductivity followed by a slight decrease, which may be due to the occurrence of a physical adsorption of H_2S gas on the surface of the chitosan after consumption the amount of cadmium ions loaded on the surface, which led to this decrease till reaching a state of stability which expresses the saturation of the film with H_2S gas.

On the other hand, in the dark a significant decrease in electrical conductivity from 0.0035 to below 0.0030 $\Omega^{-1}m^{-1}$, this is may be due to the more activity of cadmium sulfide in light than in the dark.

3.2.3. Influence of gas concentration and limit of detection

To determine the effect of H_2S gas concentration on the electrical conductivity of the chitosan film, this is done by passing different concentrations of gas every ten 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. 6, shows the relationship between the change in gas concentration and the change in conductivity.

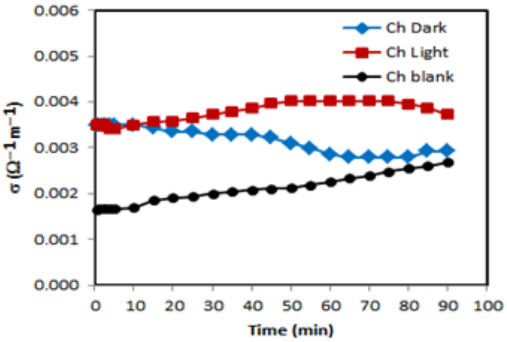

Fig. 5: Electrical conductivity vs time of adsorption of H_2S gas on the chitosan films with cadmium ions in dark and light.

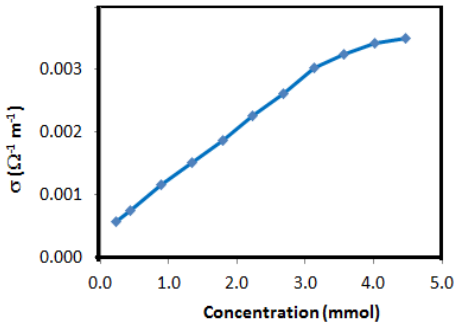

Fig. 6: Relation between concentration of hydrogen sulfide gas and electrical conductivity.

The electrical conductivity increases with the amount of H_2S gas until a steady state (limit of gas concentration detection), which mean the saturation of the film with gas and the completion of the reaction of all cadmium ions loaded on the chitosan film.

3.3. Characterization of film samples after gas detection

3.3.1 Scanning Electron Microscope (SEM)

Fig. 7, shows the scanning electron microscopy (SEM) images of Ch, ChH_2S, ChCd and ChCdS films, We can see that, relative to (Ch) film as a blank, the other three films (ChH_2S, ChCd and ChCdS) is clearly been different. The SEM images show that the samples obtained consists of different films of (Ch, ChH_2S, ChCd and ChCdS), at accelerating voltage 15 kV and magnification 3,000X. More details of distribution thickness and softness were obtained from images.

3.3.2. Resistor–capacitor circuit (R-C circuit) tests:

From the R-C circuit, possible to obtain the time constant (**τ**) of the circuit, which is the time required for the voltage on both sides of the capacitor to reach 0.37 of its maximum value, from the following relationships [49]:

$$V_c = V_o\, e^{-\frac{t}{RC}} \qquad (3)$$

$$lnV_c = lnV_o - \frac{t}{RC} \qquad (4)$$

$$\tau = RC \qquad (5)$$

where V_o, V_c were initial and variable voltages respectively, R is the resistance of sample, C is the capacity of the capacitor (220 μF, 16 V), and t is the time.

The potential difference between the two sides of the capacitor were measured at time intervals and draw the relationship between V_c with time to find the time constant (Fig. 8), and the results obtained are recorded in Table 1. By comparing the results, it was noticed that the time constant and resistance values vary between the samples under study. Decline in the time constant and resistance values this mean increasing electrical conductivity of the samples.

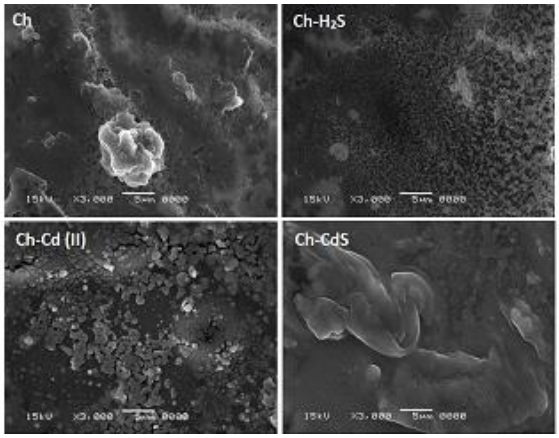

Fig.7: SEM of chitosan films in absence and presence of Cd ionsand/or H_2S gas.

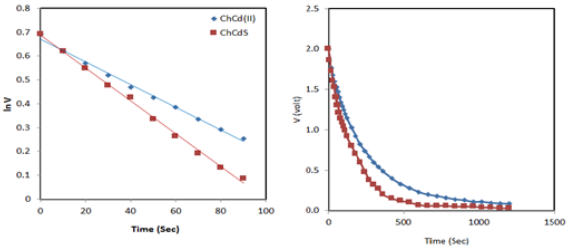

Fig. 8 : R-C Relationships

4. Conclusion

This work is very important for a human health due to detection of hydrogen sulfide gas by the prepared film. In this study after prepared and characterized chitosan by thermo gravimetric analysis (TGA), FT-IR spectroscopic analyses, and scanning electron microscopy (SEM), functionalized chitosan

films has 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; in (Ch) blank a slight increase in electrical conductivity with time, the determination of electrical conductivity of cadmium- loaded chitosan films to H_2S gas in dark and light. In the light a significant increase in electrical conductivity starts from above 0.0035 to 0.0040 $\Omega^{-1}m^{-1}$. On the other hand, in the dark a significant decrease in electrical conductivity from 0.0035 to below 0.0030 $\Omega^{-1}m^{-1}$, this is may be due to the more activity of cadmium sulfide in light than in the dark. To determine the effect of H_2S gas concentration on the conductivity of the chitosan film, electrical conductivity increases with the amount of H_2S gas until a steady state. Furthermore, The films were examined after the adsorption process of gas by; resistor-capacitor circuit, and scanning electron microscopy (SEM), were used to characterize the samples.

5. References

[1] J. Jiang, A. Chan, S. Ali, A. Saha, K. J. Haushalter, W. L. M. Lam, M. Glasheen, J. Parker, M. Brenner, S. B. Mahon, H. H. Patel, R. Ambasudhan, S. A. Lipton, R. B. Pilz, G. R. Boss, Hydrogen Sulfide—Mechanisms of Toxicity and Development of an Antidote, Scientific Reports, 6 (2016) 20831.

[2] K. R. Olson, A practical look at the chemistry and biology of hydrogen sulfide, Antioxid. Redox Signaling, 17 (2012) 32-44.

[3] C. CHSJ, Hydrogen sulfide: human health aspects. World Health Organization, Geneva (2003).

[4] S. Potivichayanon, P. Pokethitiyook, M. Kruatrachue, Hydrogen sulfide removal by a novel fixed-film bioscrubber system, Process Biochem, 41 (2006) 708–715.

[5] A. M. EL-Shamy, F. M. Alkharafi, R. M. Abdallah, I. M. Ghayad, Electrochemical Oxidation of Hydrogen Sulfide in Polluted Brines Using Porous Graphite Electrodes under Geothermal Conditions, Chemical Science Journal 2010, (2010) 1-12.

[6] B. G. Ateya, F. M. Alkharafi, A. M. EL-Shamy, A. Y. Saad, R. M. Abdalla, Electrochemical desulfurization of geothermal fluids under high temperature and pressure, J Appl Electrochem, 39 (2009) 383-389.

[7] F. M. Alkharafi, A. M. EL-Shamy, B. G. Ateya, Effect of 3-aminotriazole on the Corrosion of Copper in Polluted and Unpolluted Media, Journal of Chemistry and Chemical Engineering, 3(10) (2009) 42-50+56.

[8] A. M. EL-Shamy, S. T. Gaballah, A. E. El Meleigy, Inhibition of Copper Corrosion in The Presence of Synthesized (E)-2-(4-Bromophenoxy)-N´-(2,4-Dihydroxybenzylidene) Acetohydrazide in Polluted and Unpolluted Salt Water, International Journal of Recent Development in Engineering and Technology, 1(2) (2013) 1-11.

[9] A. M. EL-Shamy, A. M. A. Elkareim, A. Kalmouch, Mitigation of Sulfide Attach on α-Brass Surface by Using Sodium (Z) -4-Oxo-4-P-Tolyl-2-Butenoate, J Chem Eng. Process Technol, 7 (2016) 1.

[10] M. M. Megahed, M. Youssif, A. M. EL-Shamy, Selective Formula as A Corrosion Inhibitor to Protect the Surface of Antiquities Made of Leather-Composite Brass Alloy, Egypt. J. Chem., 63(12) (2020) 5269-5287.

[11] A. M. EL-Shamy, K. M. Zohdy, Corrosion Resistance of Copper in Unpolluted and Sulfide Polluted Salt Water by Metronidazole, Journal of Applied Chemical Science International, 2 (2) (2015) 56-64.

[12] A. V. Dubinin, T. P. Demidova, V. V. Kremenetskii, N. M. Kokryatskaya, M. N. Rimskaya_Korsakova, E. V. Yakushev, Determination of the Reduced Sulfur Species in the Anoxic Zone of the Black Sea: A Comparison of the Spectrophotometry and Iodometry Techniques, Oceanology, 52 (2012) 181–190.

[13] W. Ciesielski, R. Zakrzewski, Iodometric titration of sulfur compounds in alkaline medium, Chem. Anal., 51 (2006) 653-678.

[14] Z. Guo, G. Chen, G. Zeng, Z. Li, A. Chen, J. Wang, L. Jiang, Fluorescence chemosensors for hydrogen sulfide detection in biological systems, Analyst, 140 (2015) 1772–1786.

[15] S. Singha, D. Kim, H. Moon, T. Wang, K. H. Kim, Y. H. Shin, J. Jung, E. Seo, S. J. Lee, K. H. Ahn, Toward a Selective, Sensitive, Fast-Responsive, and Biocompatible Two-Photon Probe for Hydrogen Sulfide in Live Cells, Anal. Chem., 87 (2015) 1188–1195.

[16] Z. Dai, L. Tian, B. Song, Z. Ye, X. Liu, J. Yuan, Ratiometric Time-Gated Luminescence Probe for Hydrogen Sulfide Based on Lanthanide Complexes, Anal. Chem., 86 (2014) 11883–11889.

[17] N. Adarsh, M. S. Krishnan, D. Ramaiah, Sensitive Naked Eye Detection of Hydrogen Sulfide and Nitric Oxide by Aza-BODIPY Dyes in Aqueous Medium, Anal. Chem., 86 (2014) 9335–9342.

[18] J. Hao, B. Xiong, X. D. Cheng, Y. He, E. S. Yeung, High-Throughput Sulfide Sensing with Colorimetric Analysis of Single Au–Ag Core–Shell Nanoparticles, Anal. Chem., 86 (2014) 4663–4667.

[19] Y. Y. Zhang, H. Zhou, P. Wu, H. R. Zhang, J. J. Xu, H. Y. Chen, In Situ Activation of CdS Electrochemiluminescence Film and Its Application in H_2S Detection, Anal. Chem., 86 (2014) 8657–8664.

[20] X. Shen, E.A. Peter, S. Bir, R. Wang, C.G. Kevil, Analytical measurement of discrete hydrogen sulfide pools in biological specimens, Free Radical Biol. Med., 52 (2012) 2276-2283.

[21] M. D. Levitt, M. S. Abdel-Rehim, J. Furne, Free and acid-labile hydrogen sulfide concentrations in

mouse tissues: anomalously high free hydrogen sulfide in aortic tissue, Antioxid. Redox Signaling, 15 (2011) 373-378.
[22] J. Chen, J. Gu, R. Zhang, Y. Mao, S. Tian, Freshness Evaluation of Three Kinds of Meats Based on the Electronic Nose, Sensors, 19 (2019) 605.
[23] S. Singkammo, A. Wisitsoraat, C. Sriprachuabwong, A. Tuantranont, S. Phanichphant, C. Liewhiran, Electrolytically Exfoliated Graphene-Loaded Flame-Made Ni-Doped SnO2 Composite Film for Acetone Sensing, ACS Appl. Mater. Interfaces, 7 (2015) 3077–3092.
[24] K. Suematsu, Y. Shin, Z. Hua, K. Yoshida, M. Yuasa, T. Kida, K. Shimanoe, Nanoparticle Cluster Gas Sensor: Controlled Clustering of SnO2 Nanoparticles for Highly Sensitive Toluene Detection, ACS Appl. Mater. Interfaces, 6 (2014) 5319–5326.
[25] S. Jana, A. Mondal, Fabrication of SnO2/α-Fe2O3, SnO2/α-Fe2O3–PB Heterostructure Thin Films: Enhanced Photodegradation and Peroxide Sensing, ACS Appl. Mater. Interfaces, 6 (2014) 15832–15840.
[26] J. Huang, Y. Zhu, H. Zhong, X. Yang, C. Li, Dispersed CuO Nanoparticles on a Silicon Nanowire for Improved Performance of Nonenzymatic H2O2 Detection, ACS Appl. Mater. Interfaces, 6 (2014) 7055–7062.
[27] F. Fan, Y. Feng, P. Tang, A. Chen, R. Luo, D. Li, Synthesis and Gas Sensing Performance of Dandelion-Like ZnO with Hierarchical Porous Structure, Ind. Eng. Chem. Res., 53 (2014) 12737–12743.
[28] S. G. Surya, S. Bhanoth, S. M. Majhi, Y. D. More, V. M. Teja, K. N. Chappanda, A silver nanoparticle-anchored UiO-66(Zr) metal–organic framework (MOF)-based capacitive H_2S gas sensor, CrystEngComm, 21 (2019) 7303–7312.
[29] T. Sauerwald, J. Hennemann, C. D. Kohl, T. Wagner, S. Russ, H_2S detection utilizing percolation effects in copper oxide, in: Proc. AMA Conf. Sensor, (2013) 656–660.
[30] J. Kneer, J. Wöllenstein, S. Palzer, Specific, trace gas induced phase transition in copper(II)oxide for highly selective gas sensing, Appl. Phys. Lett., 105 (2014) 073509.
[31] F. I. M. Ali, S. T. Mahmoud, F. Awwad, Y. E. Greish, A. F. S. Abu-Hani, Low power consumption and fast response H_2S gas sensor based on a chitosan-CuO hybrid nanocomposite thin film, Carbohydrate Polymers, 236 (2020) 116064.
[32] R. Kumar, H. Rahman, S. Ranwa, A. Kumar, G. Kumar, Development of cost effective metal oxide semiconductor based gas sensor over flexible chitosan/PVP blended polymeric substrate, Carbohydrate Polymers, 239 (2020) 116213.
[33] B. Liu, S. Wang, Z. Yuan, Z. Duan, Q. Zhao, Y. Zhang, Y. Su, Y. Jiang, G. Xie, H. Tai, Novel chitosan/ZnO bilayer film with enhanced humidity-tolerant property: Endowing triboelectric nanogenerator with acetone analysis capability, Nano Energy, 78 (2020) 105256.
[34] M. F. Shukur, M. F. Z. Kadir, Hydrogen ion conducting starch-chitosan blend based electrolyte for application in electrochemical devices, Electrochim. Acta, 158 (2015) 152–165.
[35] S. Monisha, T. Mathavan, S. Selvasekarapandian, A. Milton, F. Benial, G. Aristatil, N. Mani, M. Premalatha, D. V. Pandi, Investigation of biopolymer electrolyte based on cellulose acetate-ammonium nitrate for potential use in electrochemical devices, Carbohydr. Polym., 157 (2017) 38–47.
[36] H. El Knidri, R. Belaabed, A. Addaou, A. Laajeb, A. Lahsini, Extraction, chemical modification and characterization of chitin and chitosan, International Journal of Biological Macromolecules, 120 (2018)1181-1189.
[37] M. Rinaudo, Chitin and chitosan: Properties and applications, Prog. Polym. Sci., 31 (2006) 603–632.
[38] A. Varma, S. Deshpande, J. Kennedy, Metal complexation by chitosan and its derivatives: a review, Carbohydr. Polym., 55 (2004) 77–93.
[39] A. Yu. Mironenko, A. A. Sergeev, A. E. Nazirov, E. B. Modin, S. S. Voznesenskiy, S. Y. Bratskaya, H_2S Optical Waveguide Gas Sensors Based On Chitosan/Au And Chitosan/Ag Nanocomposites, Sensors and Actuators B : Chemical, 225 (2016) 348-353.
[40] B. Liu, G. Xie, C. Li, S. Wang, Z. Yuan, Z. Duan, Y. Jiang, H. Tai, A chitosan/amido-graphene oxide-based self-powered humidity sensor enabled by triboelectric effect, Rare Met., 8 (2021) 1995–2003.
[41] P. Qi, Z. Xu, T. Zhang, T. Fei, R. Wang, Chitosan wrapped multiwalled carbon nanotubes as quartz crystal microbalance sensing material for humidity detection, Journal of Colloid and Interface Science, 560 (2020) 284–292.
[42] P. Qi, Z. Xu, T. Zhou, T. Zhang, H. Zhao, Study on a quartz crystal microbalance sensor based on chitosan-functionalized mesoporous silica for humidity detection, Journal of Colloid and Interface Science, 583 (2021) 340–350.
[43] E. Comini, G. Faglia, G. Sberveglieri, Solid State Gas Sensing, Springer Science & Business Media, LLC., (2009).
[44] Y. S. Puvvada, S. Vankayalapati, S. Sukhavasi, Extraction of chitin from chitosan from exoskeleton of shrimp for application in the pharmaceutical industry, Int Curr Pharm J, 9 (2012) 258-263.
[45] Y. Wan, H. Wu, A. Yu, D. Wen, Biodegradable polylactide/chitosan blend membranes, Biomacromolecules, 7 (2006) 1362-1372.
[46] H. Jiang, J. Liang, J. T. Grang, W. Su, T. J. Bunning, T. M. Cooper, W. W. Adams, Characterization of chitosan and rare-earth-metal-ion doped chitosan films. Macromol. Chem. Phys., 198 (1997) 1561-1578.
[47] C. G. T. Neto, J. A. Giacometti, A. E. Job, F. C. Ferreira, J. L. C. Fonseca, M. R. Pereira, Thermal analysis of chitosan based networks. Carbohydr. Polym., 62 (2005) 97-103.
[48] J. M .Nieto, C. Peniche-Covas, G. Padron, Characterization of chitosan by pyrolysis-mass spectrometry, thermal analysis and differential

scanning calorimetry. Thermochim. Acta, 176 (1991) 63-68.
[49] S. Dunford, A. Grinshpan, G. Woods, Calculating the Time Constant of an RC Circuit, Undergraduate, Journal of Mathematical Modeling, 2 (2010) 1-11.