***International Journal of Chemical and Biochemical Sciences***
***(ISSN 2226-9614)***

***Journal Home page: www.iscientific.org/Journal.html***

*© International Scientific Organization*

# The Influence of Drying Temperature on the pH Sensitivity of $TiO_2$ based Integrated All-Solid Electrodes (IASE)

***Norhidayatul Hikmee Mahzan[1,2] , Shaiful Bakhtiar Hashim[1,2] , Rosalena Irma Alip[2] , Zuhani Ismail Khan[3] , Sukreen Hana Herman[2,3,*]***

*[1]Nano-Electronic Center (NET), School of Electrical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.*

*[2] Integrated Sensors Research Lab, School of Electrical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.*

*[3]Microwave Research Institute, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.*

## Abstract

Titanium dioxide ($TiO_2$) sensing electrode and a silver/silver chloride (Ag/AgCl) reference electrode were deposited on an indium tin oxide (ITO) substrate and used as an integrated all-solid electrode (IASE) for pH sensing applications. pH sensing applications have attracted a lot of interest because they can be used in many different areas, such as monitoring the environment, aquaculture, agriculture, food inspection technology, and biomedical applications. $TiO_2$ and Ag/AgCl thin films were fabricated using the sol-gel spin coating method and a thermal evaporator. After the deposition process, the thin films were dried at room temperature, 50 ºC, and 100 ºC to study the influence of the drying process on the pH sensitivity and linearity of IASE. It was found that the sample dried at 100 ºC showed high sensitivity and linearity with 67 mV/pH and 0.9827.

**Keywords:** Drying temperature, pH sensitivity, Integrated all-solid electrodes

**Full length article** **Corresponding Author*, e-mail: hana1617@uitm.edu.my

## 1. Introduction

In recent times, researchers have shown increasing interest in pH sensors, aiming to explore their maximum potential in a range of applications such as agriculture, health monitoring, food processing, and environmental observation [1-6]. Due to its high sensitivity and accuracy, the preferred method for determining pH levels is currently using a glass electrode. However, the main disadvantage of using glass electrodes is their mechanical fragility. Being built of glass makes them difficult to miniaturize and susceptible to breakage, which restricts their use in some applications. Moreover, this glass electrode requires an internal solution for it to work. This internal solution is susceptible to foreign ionic contamination and needs high maintenance [7]. In response to the challenges posed by glass electrodes' fragility and maintenance requirements, a MOSFET-based pH sensor was developed and named the ion-sensitive field effect transistor (ISFET) in 1972 by P. Bergveld [8]. This new solid-state device enabled the measurement of ionic reactions in electrochemical and biological environments.

However, during the measurement process, the ISFET had some limitations in dealing with temperature, light, and ionic penetration issues. In 1983, Spiegel [9] proposed a solution to these issues through the extended gate field effect transistor (EGFET) detection method. The EGFET pH sensor offered several advantages over the ISFET, such as good stability during the measurement process under varying light and temperature conditions, high sensitivity, low impedance, low cost, and simple packaging [10]. Various metal oxides, including tantalum oxide ($Ta_2O_5$), titanium dioxide ($TiO_2$), copper oxide (CuO), zinc oxide (ZnO), and tin oxide ($SnO_2$), have been utilized in various applications [11-15]. Among these, $TiO_2$ has emerged as the most promising material with numerous applications, such as memristors, dye-sensitized solar cells, photocatalysts, capacitors, gas sensors, and pH-sensing electrodes [16-18]. As a sensing electrode, $TiO_2$ offers good chemical stability, sturdiness, flexibility, and a high dielectric constant [17-19].

Several methods have been reported for fabricating $TiO_2$ sensing electrodes, such as physical and chemical vapor deposition, sputtering, immersion techniques, spin coating, spray pyrolysis, electron beam deposition, and pulsed laser deposition methods. Among all these techniques, the sol-gel spin coat method is the simplest and most cost-effective, delivering a homogeneous chemical reaction between the thin films and substrate, especially at high temperatures [20-21]. Thus, in this work, we present the study of the drying temperature effect on integrated all solid electrodes (IASE) for extended gate field effect transistor (EGFET) pH sensing application. In addition, the EGFET sensor was characterized for its transfer characteristic to analyze the sensitivity and linearity of IASE.

## 2. Materials and methods

### *2.1 Sample preparation*

The IASE was prepared with a sensing electrode (SE) and a reference electrode (RE) fabricated on a single substrate of indium tin oxide (ITO) coated glass. **Figure 1** shows the top view configuration of IASE, the area for both $TiO_2$ SE and Ag/AgCl RE is 0.35 $cm^2$ separated by a 0.6 $cm^2$ insulation area. The insulation area was formed by etching the ITO-coated glass substrate using hydrochloric acid (HCl) and zinc powder to remove the conductive ITO layer to prevent an electrical connection between SE and RE. Before the fabrication of the IASE, the ITO substrate underwent ultrasonic cleaning using Hwashin Technology Powersonic 405. The cleaning process involved using a solution of ethanol and deionized water for 10 minutes each, then drying the substrate using inert nitrogen gas. To prepare the $TiO_2$, a mixture of Solution A and Solution B was used. Solution A was composed of absolute ethanol as a solvent, glacial acetic acid as a stabilizer or chelating agent to control the hydrolysis reaction of alkoxides, and titanium (IV) isopropoxide as the precursor. On the other hand, Solution B contained a mixture of absolute ethanol, Triton X-100 as a surfactant, and deionized water. Solutions A and B were prepared separately and stirred for an hour before being mixed and stirred for another hour at room temperature.

To produce a $TiO_2$ thin film from the prepared $TiO_2$ solution, the sol-gel spin coater (Laurell Model WS-650MZ-8NPP/LITE) was used. This spin-coating technique has reportedly produced a uniform thin film. The deposition process started with positioning the clean ITO substrate on the spin coater chuck. Then followed by dropping ten drops of $TiO_2$ solution on the substrate. The substrate was initially rotated at 500 rpm for 10 seconds before the rotational speed increased to 3000 rpm for one minute. The high-speed spinning will cause the solution to be evenly dispersed throughout the surface of the substrate resulting in a thin film with uniform thickness. The thin film was then dried at 100 °C for 10 minutes to remove solvents such as water and ethanol, leaving a pure $TiO_2$ thin film. After drying, the sample was annealed at 400 °C for 15 minutes. This complete process produced a single layer of $TiO_2$ thin film on the substrate with a thickness of approximately around 23 nm. The Ag layer was deposited using a thermal evaporator (TE), which is a commonly used method for depositing thin metal films.

In this process, the Ag material is heated to a high temperature, causing it to evaporate and condense onto the substrate in a thin film form. The thickness of the Ag layer was controlled to be approximately 300 nm. After the deposition process, a 5-second chlorination process was carried out using $FeCl_3$ to form Ag/AgCl RE. This process involves the reaction between Ag and $FeCl_3$, forming AgCl on the surface of the Ag layer. The Ag/AgCl reference electrode provides a stable potential for pH-sensing measurement.

### *2.2 Measurement setup*

**Figure 2** shows the EGFET measurement setup consisting of IASE connected to the semiconductor device analyzer (SDA). In addition, the silver/silver chloride (Ag/AgCl) RE was connected to SMU 3, while the $TiO_2$ SE was connected to the pin gate of commercialized CD40007UBE MOSFET as the extended gate sensing electrode. Commercial pH buffer solutions were utilized to investigate the sensor reaction capabilities further. IASE was submerged in several pH buffer solutions (2, 4, 7, 10, and 12). The transfer characteristic (drain current, $I_D$ versus reference voltage, $V_{REF}$) and output characteristic (drain current, $I_D$ versus drain-source voltage, $V_{DS}$) were obtained from this measurement. The sensitivity of the fabricated IASE was estimated by plotting the graph of the reference voltage at drain current, $I_D$ at 100 μA versus pH level.

## 3. Results and Discussions

**Figure 3 (a)** shows the transfer characteristic for IASE at room temperature in different buffer solutions of pH 2, pH 4, pH 7, pH 10, and pH 12, while **Figure 3 (b)** shows the graph of output voltage versus pH value. The sensitivity and linearity value was extracted from the slope and regression value of the graph in **Figure 3 (b)**. The value of $V_{REF}$ was measured at 100 μA of drain current. As a result, the sensitivity and linearity of IASE at room temperature were around 66.1 mV/pH and 0.9561, respectively. This value was more than the Nernstian theoretical response at 59 mV/pH. As the drying temperature increased to 50 °C, the sensitivity increased to 67.3 mV/pH, but the linearity slightly decreased to 0.9211, as seen in **Figures 4 (a)** and **(b)**. Finally, further increasing the drying temperature to 100 °C, the sensitivity was recorded with no dramatic changes in sensitivity and linearity with 67 mV/pH and 0.9827, respectively. The detailed value is tabulated in **Table 1**.

The transfer characteristic result shown in **Figures 3 (a)** to **5 (a)** relates to the site binding theory, which describes the pH sensing process of a gate electrode's oxide surface. When immersed in a solution, a metal oxide surface can either donate or receive a proton, resulting in a net positively or negatively charged surface [22]. **Figure 6** depicts the basic reaction on the metal oxide surface, which generates surface potential under neutral, acidic, and alkaline circumstances. The surface of metal oxide has a hydroxyl group, as shown in **Figure 6**, and these hydroxyl groups are capable of interacting with pH potential determining ions (PDI), which are hydrogen ions (in acidic solution) and hydroxide ions (in basic solution). Therefore, the surface of the sensing membrane will be more positively or negatively charged depending on the type of PDI that is prominent in the solution.

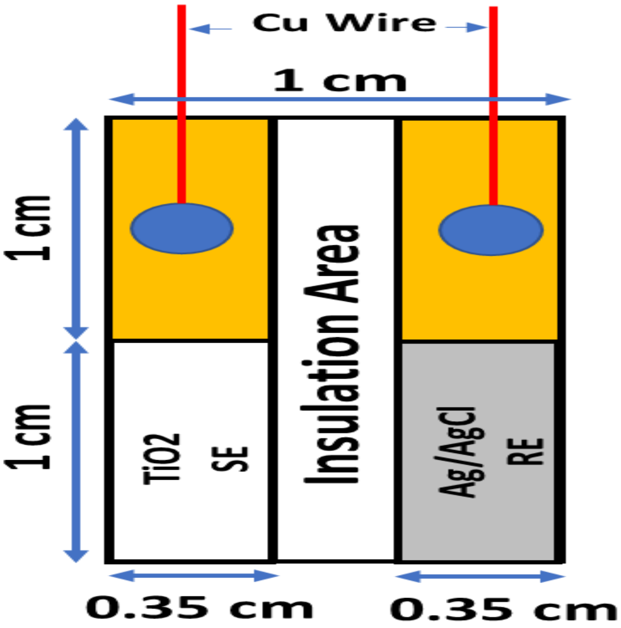

**Figure 1.** Top view configuration of IASE

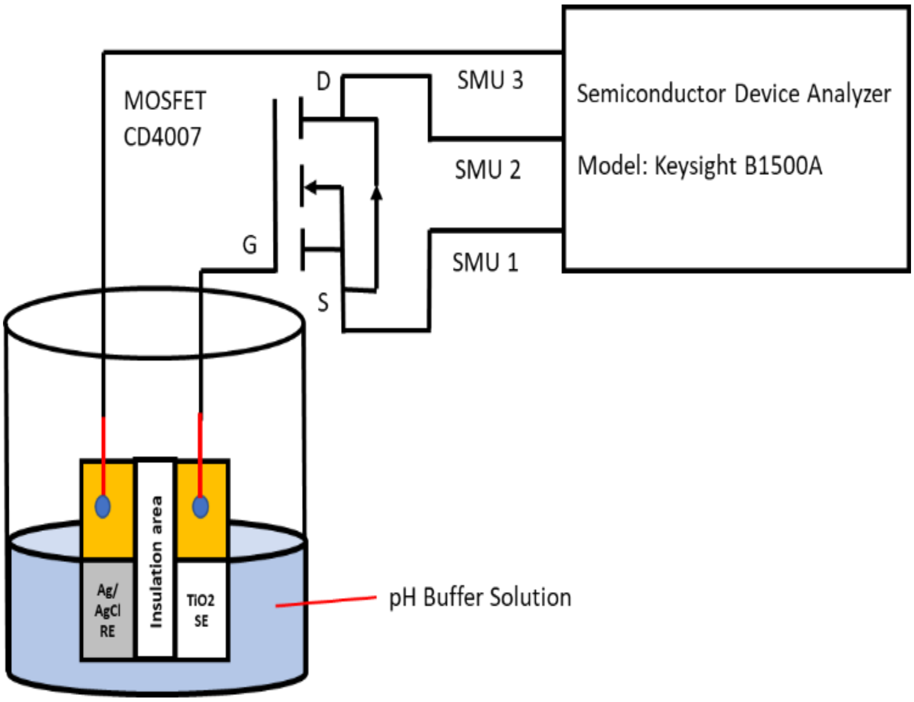

**Figure 2.** EGFET measurement setup

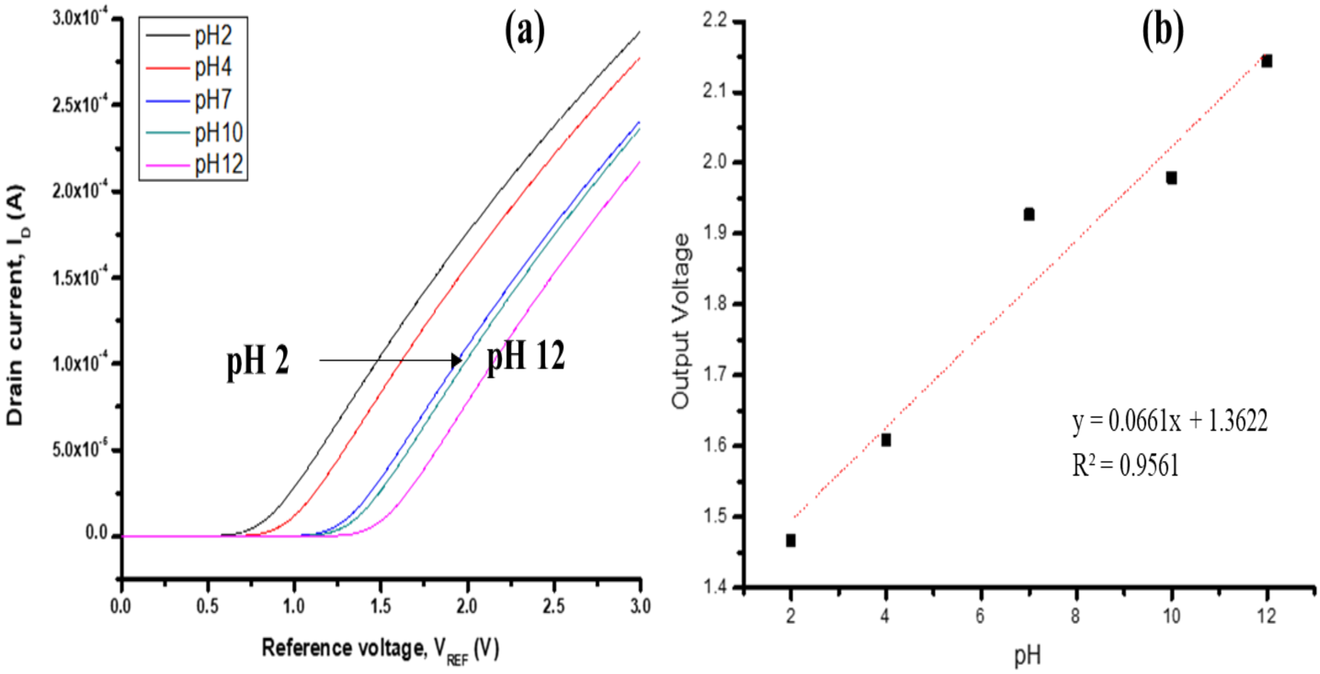

**Figure 3.** (a) Transfer characteristic ($I_D$ versus $V_{REF}$) for fabricated IASE at room temperature and (b) The graph of output voltage versus pH value

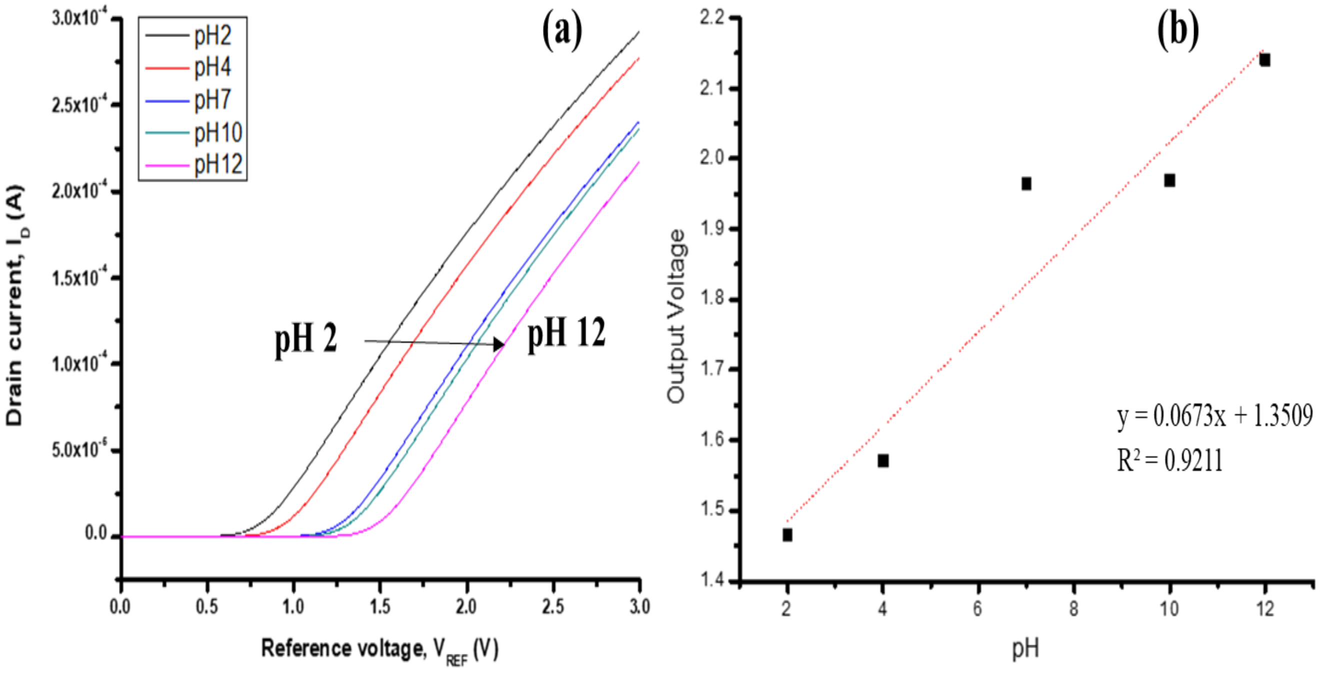

**Figure 4.** (a) Transfer characteristic ($I_D$ versus $V_{REF}$) for fabricated IASE at 50 ºC and (b) The graph of output voltage versus pH value

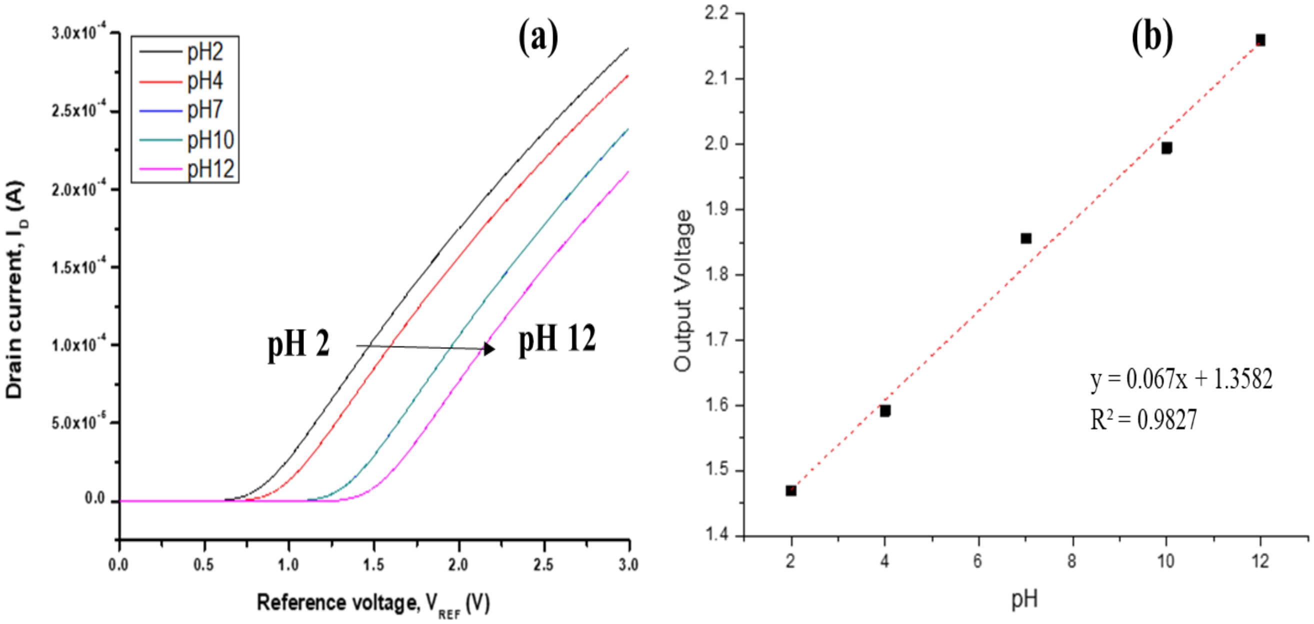

**Figure 5.** (a) Transfer characteristic ($I_D$ versus $V_{REF}$) for fabricated IASE at 100 °C and (b) The graph of output voltage versus pH value

**Table 1.** Sensitivity and linearity value of IASE

| **Materials** | **RT** | **50 °C** | **100 °C** |
|---|---|---|---|
| Sensitivity (mV/pH) | 66.1 | 67.3 | 67 |
| Linearity | 0.9561 | 0.9211 | 0.9827 |

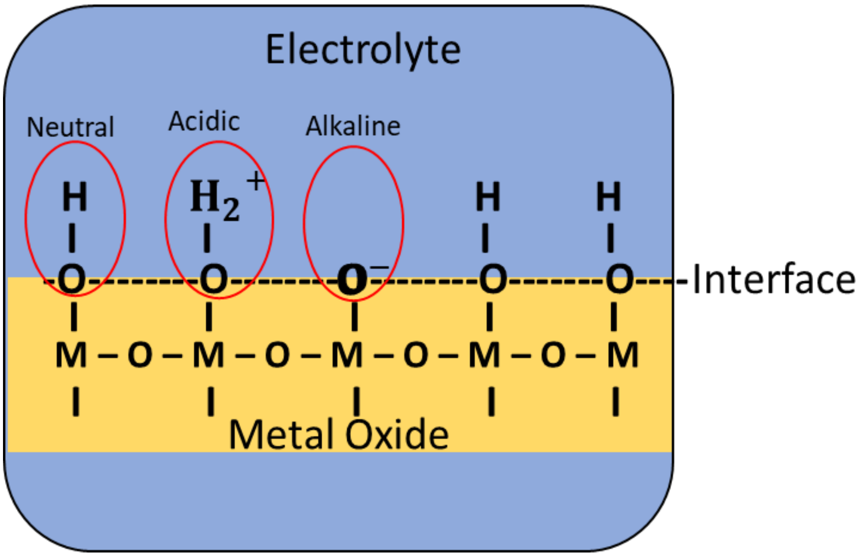

**Figure 6.** Basic reaction on metal oxide surface ion's in neutral, acidic and alkaline.

## 4. Conclusions

In conclusion, the IASE-based $TiO_2$ sensing and Ag/AgCl reference electrodes have been successfully fabricated on an ITO-coated glass substrate. The deposited IASE has been proven to be sensitive to pH. Furthermore, increasing drying temperature has improved both sensitivity and linearity of the IASE. This work's highest sensitivity and linearity were 67.3 mV/pH and 0.9827. As a future recommendation, research will be conducted on the various IASE-based flexible substrates.

**Acknowledgment**

This work was supported by the Ministry of Higher Education Malaysia under the Fundamental Research Grant Scheme under the [Project Code: FRGS/1/2021/TK0/UITM/02/50].

## References

[1] L. Gao, P. Liu, L. Liu, S. Li, Y. Zhao, J. Xie, & H. Xu. (2022). κ-carrageenan-based pH-sensing films incorporated with anthocyanins or/and betacyanins extracted from purple sweet potatoes and peels of dragon fruits. Process Biochemistry. 121: 463-480.

[2] Z. Güngör, & H. Ozay. (2022). Ultra-fast pH determination with a new colorimetric pH-sensing hydrogel for biomedical and environmental applications. Reactive and Functional Polymers. 180: 105398.

[3] C. Nicolò, M. Parmeggiani, S. Villata, D. Baruffaldi, S. L. Marasso, G. Canavese, ... & F. Frascella. (2022). A programmable culture platform for hydrostatic stimulation and in situ pH sensing of lung cancer cells with organic electrochemical transistors. Micro and Nano Engineering. 16: 100147.

[4] J. Chalitangkoon, & P. Monvisade. (2021). Synthesis of chitosan-based polymeric dyes as colorimetric pH-sensing materials: Potential for food and biomedical applications. Carbohydrate Polymers. 260: 117836.

[5] M. Fathi, A. Babaei, & H. Rostami. (2022). Development and characterization of locust bean gum-Viola anthocyanin-graphene oxide ternary nanocomposite as an efficient pH indicator for food packaging application. Food Packaging and Shelf Life. 34: 100934.

[6] L. Jovanska, C. H. Chiu, Y. C. Yeh, W. D. Chiang, C. C. Hsieh, & R. Wang. (2022). Development of a PCL-PEO double network colorimetric pH sensor using electrospun fibers containing Hibiscus rosa sinensis extract and silver nanoparticles for food monitoring. Food Chemistry. 368: 130813.

[7] A. Sardarinejad, D. K. Maurya, & K. Alameh. (2015). The pH sensing properties of RF sputtered RuO2 thin-film prepared using different Ar/O2 flow ratio. Materials. 8 (6): 3352-3363.

[8] P. Bergveld. (1972). Development, operation, and application of the ion-sensitive field-effect transistor as a tool for electrophysiology. IEEE Transactions on Biomedical Engineering. (5): 342-351.

[9] I. Lauks, P. Chan, & D. Babic. (1983). The extended gate chemically sensitive field effect transistor as multi-species microprobe. Sensors and Actuators. 4: 291-298.

[10] N. Mokhtarifar, F. Goldschmidtboeing, & P. Woias. (2019). ITO/glass as extended-gate of FET: A low-cost method for differential pH-sensing in alkaline solutions. Journal of The Electrochemical Society. 166 (12): B896.

[11] N. Sharma, M. Kumar, N. Kumari, A. Deep, J. K. Goswamy, & A. L. Sharma. (2020). Tantalum oxide thin films for electrochemical pH sensor. Materials Research Express. 7 (3): 036405.

[12] H. A. Khizir, & T. A. H. Abbas. (2022). Hydrothermal synthesis of TiO2 nanorods as sensing membrane for extended-gate field-effect transistor (EGFET) pH sensing applications. Sensors and Actuators A: Physical. 333: 113231.

[13] N. P. Shetti, S. D. Bukkitgar, K. R. Reddy, C. V. Reddy, & T. M. Aminabhavi. (2019). ZnO-based nanostructured electrodes for electrochemical sensors and biosensors in biomedical applications. Biosensors and Bioelectronics. 141: 111417.

[14] T. Ramakrishnappa, K. Sureshkumar, & M. Pandurangappa. (2020). Copper oxide impregnated glassy carbon spheres based electrochemical interface for nitrite/nitrate sensing. Materials Chemistry and Physics. 245: 122744.

[15] H. R. Sadig, L. Cheng, & T. fei Xiang. (2019). Synthesis of tetra-metal oxide system based pH sensor via branched cathodic electrodeposition on different substrates. Arabian Journal of Chemistry. 12 (5): 610-620.

[16] A. M. Tayeb, A. A. Solyman, M. Hassan, & T. M. A. el-Ella. (2022). Modeling and simulation of dye-sensitized solar cell: Model verification for different semiconductors and dyes. Alexandria Engineering Journal. 61 (12): 9249-9260.

[17] M. A. Zulkefle, S. H. Herman, R. A. Rahman, K. A. Yusof, A. B. Rosli, W. F. Hanim Abdullah, & Z. Zulkifli. (2021). Evaluation on the EGFET pH sensing performance of sol-gel spin coated titanium dioxide thin film. Jurnal teknologi. 83 (4): 119-125.

[18] X. Wang, C. Jin, J. K. Eshraghian, H. H. C. Iu, & C. Ha. (2021). A behavioral spice model of a binarized memristor for digital logic implementation. Circuits, Systems, and Signal Processing. 40: 2682-2693.

[19] C. Chen, Y. Zhang, H. Gao, K. Xu, & X. Zhang. (2022). Fabrication of Functional Super-Hydrophilic TiO2 Thin Film for pH Detection. Chemosensors. 10 (5): 182.

[20] M. A. Zulkefle, R. A. Rahman, K. A. Yusoff, W. F. H. Abdullah, M. Rusop, & S. H. Herman. (2016). Post-deposition annealing temperature dependence TiO2-based EGFET pH sensor sensitivity. In AIP Conference Proceedings (Vol. 1733, No. 1). AIP Publishing.

[21] L. Scrimieri, A. Serra, D. Manno, P. Alifano, S. M. Tredici, M. Calcagnile, & L. Calcagnile. (2019). TiO2 films by sol-gel spin-coating deposition with

microbial antiadhesion properties. Surface and Interface Analysis. 51 (13): 1351-1358.

[22] L. H. Jiao, & N. Barakat. (2013). Ion-sensitive field effect transistor as a pH sensor. Journal of Nanoscience and Nanotechnology. 13 (2): 1194-1198.